SYNTEX agribusiness inc NUTRITION AND CHEMICAL DIVISION ENVIRONMENTAL PROJECTS DEPARTMENT

March 5, 1991

Mr. Glenn Curtis
U.S. Environmental Protection Agency
Region VII
726 Minnesota Avenue
Kansas City, KS 66101

Re: Verona Fish and Sediment Plan

Dear Glenn:

Enclosed are materials concerning the levels of 2,3,7,8-Tetrachlorodibenzo-p-dioxin ("dioxin") in fish collected from the Spring River downstream from the Syntex Agribusiness, Inc. ("Syntex") plant in Verona, Missouri. As we discussed during our conference call on November 29, 1990, the levels of dioxin found in fish obtained from the Spring River in 1990 are the lowest recorded during the seven years of the project.

The enclosed information is submitted in accordance with: (1) the September 9, 1983 Consent Agreement and Order ("Order") between Syntex and the U.S. Environmental Protection Agency ("EPA"); (2) the Verona Fish and Sediment Plan ("Plan"); and (3) the terms of a one year extension of the sampling and analysis program as expressed in letters between Syntex and EPA dated July 17, 1990 and October 3, 1990. The enclosures include the annual report of fish samples taken from the Spring River in 1990, the statistical analysis of those samples and samples taken in previous years, and a statistical report that summarizes the conclusions drawn from the analysis.

The annual analytical report documents the origins of the samples and the method of analysis, as discussed in the October 3, 1990 memorandum from Dr. Chan et al. to Dr. David Robertson. Table 1 of the report sets out the concentrations of dioxin detected in the fish fillets.

The statistical analysis ("Statistical Analysis of Dioxin Data From Spring River - Statistical Package", dated November 12, 1990) considers the data summarized in the 1990 annual report along with the fish data for Sites 1 and 2 contained in the annual reports for 1984 through 1989. The statistical analysis also considers the 1990 data with data collected since remediation of the Verona plant was initiated in 1987. This is a particular important time frame since the presumed source(s) of dioxin contamination of the Spring River were removed during this remedial effort. Finally, the statistical report, dated December 14, 1990, considers the results of the statistical analysis in light of the criteria set forth in the Order and Plan.

The Order provides that the initial five year sampling and analysis project may be extended if there is no statistically significant decrease in the fish results at Site 1, or when a statistically significant aggregate increase in the fish results has been observed at all other sampling points. As set forth in more detail in the statistical analysis and report, there has been a significant decrease in the levels of dioxin in fish obtained from Site 1. The data gathered at Site 1 during and after the Verona remedial effort show dramatic decreases in dioxin levels. The Final Progress Report, which discussed the results obtained during the initial five year study, and the 1989 statistical report demonstrated that there has been no statistically significant aggregate increase in the fish results from Sites 2 through 5 and from Sites 2 through 4, respectively. For 1990, the data from Site 2 show dioxin levels in fish fillets that are markedly lower than any of the sampling results from prior years for Site 2. For these and other reasons, the report concludes that further sampling and analysis of Spring River fish is not warranted.

After you and your staff have had an opportunity to review the enclosed information, please contact me so that we may schedule a mutually convenient meeting or telephone conference call.

Sincerely,

SYNTEX AGRIBUSINESS, INC.

Gary J. Pendergrass By F.L.

Gary J. Pendergrass, P.E.
Manager, Environmental Projects

GJP:rlr/0818P

Enclosures

xc: Morris Kay (w/Encl.)

STATISTICAL REPORT

VERONA FISH AND SEDIMENT PLAN

DECEMBER 14, 1990

by

SYNTEX AGRIBUSINESS, INC.

Statistical Report

This statistical report ("Report") summarizes the conclusions drawn from the annual analytical report of fish samples taken from the Spring River in 1990, and from the Statistical Analysis of Dioxin Data From the Spring River ("statistical analysis"). Specifically, this Report compares the information contained in the annual report and the statistical analysis with the criteria set forth in the September 9, 1983 Consent Agreement and Order ("Order") between Syntex Agribusiness, Inc. ("Syntex") and the U.S. Environmental Protection Agency ("EPA").

This Report and the accompanying annual report and statistical analysis have been developed by Syntex in accordance with the provisions of the Order, the Verona Fish and Sediment Plan ("Plan") developed and approved under the Order, and the terms of a one year extension of the sampling and analysis program as expressed in July 17, 1990 and October 3, 1990 letters between Syntex and EPA. As discussed in the Report, additional sampling and analysis of Spring River fish under the Order is not warranted.

Background

The sampling and analysis of Spring River fish and sediment commenced in 1984 and has continued in several phases to the present time. As explained in more detail below, the initial five years of the project involved fish and sediment sampling from five locations on the Spring River. The sixth year of the project involved only fish sampling and analysis from four of the five locations on the Spring River, and this seventh year encompasses only fish sampling and analysis from two of the five locations on the Spring River.

The project was designed to monitor whether there were statistically significant increases or decreases in the levels of dioxin in the fish and sediment downstream from the Syntex Verona, Missouri, plant. Under the Order and Plan, the sampling and analysis was to extend for an initial five years, with discretionary and non-discretionary options for extending or shortening the five year program under certain specified conditions. Using its discretion under the Order, in light of the annual analytical and statistical results, EPA has progressively cut back on the extent of the sampling program since the end of the initial five year period.

The conditions under which EPA may extend the five year program are set out in paragraph 42 of the Order. Paragraph 42 provides, in part, that:

> "EPA may extend the initial five (5) year period at one year intervals and at twelve (12) mile increments for up to 5 years past this initial sampling period when no statistically significant decrease in the fish results has been observed at the 0.3 mile location downstream...or when a statistically significant aggregate increase in the fish results has been observed at all other sampling points...Sediment sampling...may be extended by EPA at one (1) year intervals and at 12 mile increments if there is a statistically significant increase in sediment results at the

0.3 mile location or a statistically significant aggregate increase in sediment results at all other sampling points."

The Plan establishes a significance level of 0.05 (or 95%) for data pertaining to Site 1.

As provided by the Order and Plan, samples of fish were obtained annually from 1984-1988 from five locations in the Spring River. In accordance with paragraph II of the Plan, fish samples were taken 0.3 miles downstream from the confluence of the Slough Area and the Spring River (Site 1); 3.0 miles downstream (Site 2); 6.0 miles downstream (Site 3); 9.0 miles downstream (Site 4); and 12.0 miles downstream (Site 5). As also provided by the Order and Plan, sediment samples were obtained annually for the five year period from Sites 1, 3, and 5. The fish and sediment samples were collected and analyzed in accordance with the requirements of the Order and Plan, and Syntex submitted to EPA five annual reports containing the yearly results of the Spring River fish and sediment sampling and analysis.

As provided by paragraph 47 of the Order and paragraph VI of the Plan, Syntex prepared a Final Progress Report and Statistical Package, dated January 30, 1989, that assessed the fish and sediment data collected during 1984 through 1988. Based upon the statistical analysis of the data collected over the five year period, the Final Progress Report concluded that:

(1) There was neither a statistically significant decrease nor increase in the levels of dioxin in fish taken from sampling Site 1 over the five year period;

(2) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin levels in the fish taken from sampling Sites 2 through 5 over the five year period;

(3) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin in the sediment taken from Site 1 over the five year period; and

(4) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin in the sediment taken from Sites 3 and 5 over the five year period.

The Final Report emphasized that the levels of dioxin detected in the fish and sediment were extremely low. It pointed out that the dioxin levels found in the fish were actually below the sensitivity of the analytical procedure anticipated by the Plan, and that the dioxin levels were considerably below the advisory levels used by the U.S. Food and Drug Administration.

Considering the purposes of the sampling and analysis program, and the criteria set out in the Order, the Final Report concluded that additional sampling of the fish and sediment was not warranted. However, EPA requested that the program be extended for an additional year to collect and analyze only fish samples from Sites 1 through 4. Syntex agreed to this one year extension and submitted an annual report of the 1989 data on November 27,

1989, and a statistical analysis on February 21, 1990 that assessed the 1989 data in conjunction with the fish data that had been collected for Sites 1 through 4 during 1984 through 1988. Consistent with the criteria established in paragraph 42 of the Order, Syntex organized the data generated over the six year period by considering the fish sampling results at Site 1, and the fish sampling results from Sites 2 through 4. The Statistical Report for the six year period of the project concluded that:

(1) The statistical analysis demonstrated that there was neither a statistically significant decrease nor a statistically significant increase in dioxin levels in fish taken from sampling Site 1 over the six year period; and

(2) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin levels in fish taken from sampling Sites 2 through 4 over the six year period.

Again, EPA requested a one year extension of the sampling program. As reflected in Syntex' October 3, 1990 letter to Mr. Glenn Curtis, Syntex agreed to collect fish from Sites 1 and 2 and to analyze fillets from the fish samples. It is the data generated from the fish collected from Sites 1 and 2 in 1990 that is the subject of this Report and the attached statistical analysis.

Summary of the 1990 Sampling Program and Statistical Analysis

The accompanying statistical analysis was performed on data collected from Sites 1 and 2 during the past seven years, including data collected in 1990. In order to correspond to the criteria in paragraph 42 of the Order quoted above, the dioxin concentrations in fish from Site 1 were tested against the hypothesis of a decrease in dioxin levels with time using both a Jonckheere test and a Student's t (multiple linear regression) test. The resulting p-values were 0.15 and 0.07, respectively, indicating a decreasing trend over time.

The statistical analyses and reports in prior years have not considered Site 2 data separately from the data collected from other downstream Sites, and evaluation criteria for Site 2 alone are not specified in the Order. Paragraph 42 of the Order combines Site 2 with the other downstream Sites and provides that the study may be extended if there is a statistically significant increase in the fish results at these Sites considered in the aggregate. As discussed above, the Final Progress Report and the 1989 Statistical Report demonstrated that this criteria for an extension of the study had not been met at Sites 2 through 5 during the initial five year study, or at Sites 2 through 4 during the sixth year of the study. Considering the data obtained in 1990, Site 2 fish dixon levels are markedly lower than any of the sampling results from prior years for this Site. These results are, in fact, similar to previous Sites 3 and 4 dioxin concentrations which have consistently been only slightly above non-detect levels since 1985 and may represent the background dioxin level for this section of the Spring River.

The data collected in 1990 from Sites 1 and 2 was combined and analyzed for a decrease in dioxin levels over the seven year study using multiple linear regression. The corresponding p-value was 0.06, strong evidence of a decrease in concentration over the seven year sample period.

The statistical analysis also examines the potential impact of the remediation of the Verona plant upon the sampling results. A statistical analysis was performed on data collected from Sites 1 and 2 from 1987 to 1990. The dioxin-contaminated soil from the Verona plant was excavated early in the summer of 1988, before the fish and sediment samples were taken in that year. In spite of decreased power due to the smaller sample size, the results indicate a highly significant decrease in dioxin concentrations over the past four years at Site 1, at Site 2, and at both Sites combined. The resulting p-values were less than 0.05.

Conclusions

The statistical analysis documents the following conclusions concerning levels of dioxin in Spring River fish:

(1) The dioxin concentrations in fish from Site 1 reflect a decreasing trend over the seven year sampling interval. The statistical analysis using the linear regression analysis for Site 1 demonstrated 93% confidence that there is a decrease in dioxin levels in fish taken from sampling Site 1 over the past seven years. The statistical analysis using the Jonckheere test, which is very sensitive to an occasional change in the trend, demonstrated 85% confidence that there is a decrease in dioxin levels in fish taken from sampling Site 1 over the past seven years;

(2) A statistically significant decrease in dioxin levels was observed in fish fillets collected from Site 1 over the last four years following remediation of the Verona plant. The statistical analysis using the linear regression analysis for Site 1 demonstrated greater than 99% confidence that there is a statistically significant decrease in dioxin levels in fish taken from sampling Site 1 over the past four years. The statistical analysis using the Jonckheere test demonstrated 98% confidence that there is a statistically significant decrease in dioxin levels in fish taken from sampling Site 1 over the past four years;

(3) The Final Progress Report and the 1989 Statistical Report demonstrated that there has been no statistically significant increase in dioxin levels from fish taken from Sites 2 through 5, and from Sites 2 through 4, respectively. Site 2 fish dioxin levels in 1990 are markedly lower than any previous data for this Site. These results are similar to previous Site 3 and Site 4 dioxin data and may represent the background dioxin level. The statistical analysis on Site 2 data alone did not support the hypothesis that there was a statistically significant decrease in dioxin levels over the past seven years in fish taken from sampling Site 2. Because this hypothesis is not a criteria set forth in the Order, it is included in this Report for informational purposes only;

(4) A statistically significant decrease, using multiple linear regression, in Site 2 fish dioxin levels has occurred during the four years following the Verona plant remediation. The statistical analysis using the linear regression analysis for Site 2 demonstrated 97% confidence that there is a statistically significant decrease in dioxin levels in fish taken from sampling Site 2 over the past four years. The statistical analysis using the Jonckheere test demonstrated 90% confidence that there is a decrease in dioxin levels in fish taken from sampling Site 2 over the past four years. For the reasons stated in item (3) above, this conclusion is included for informational purposes only; and

(5) Analysis of Sites 1 and 2 combined demonstrated strong evidence of a decrease in dioxin concentration over the seven year study, and a statistically significant decrease in dioxin concentration during the past four years. The statistical analysis of both Sites 1 and 2 combined demonstrated 94% confidence that there is a decrease in dioxin levels in fish taken from both sampling sites over the past seven years. The analysis of both Sites combined demonstrated a better than 99% confidence level that there is a statistically significant decrease in dioxin in fish taken from both sampling sites over the past four years. For the reasons stated in item (3) above, this conclusion is included for informational purposes only.

Discussion

At this point in time, the criteria in the Order relevant to determine whether the sampling program may be extended for yet another year is the trend for dioxin assays in fish fillets taken from Site 1. A statistically significant decline in assays at Site 1 would terminate the sampling and analysis program. As shown above, the statistical analysis has shown a decline in the dioxin levels at Site 1.

It is more indicative of the success of the remedial effort to consider the sampling results obtained after remedial activities commenced at Verona and after the presumed source(s) of dioxin contamination was removed. Using the four years of 1987-1990, a statistically significant decline in dioxin levels in fish taken from Site 1 is demonstrated to a confidence level greater that 99% using linear regression and to a confidence level of 98% using the Jonckheere test. This dramatically demonstrates that levels of dioxin in the fish have declined since the remedial efforts were initiated.

The criteria under the Order for extending the program considering Site 2 is whether there is a statistically significant aggregate increase in the fish results at Sites 2 through 5. This criteria has not been met as documented by the five year Final Progress Report and by the statistical report and analysis for the sixth year of the program. The dioxin levels detected in fish taken from Site 2 during this seventh year are the lowest ever recorded. Thus, the data for Site 2 do not justify an extension of the sampling program. (It is interesting to note that the analysis of Site 2 data demonstrated a statistically significant decrease in dioxin levels over the past four years.)

Finally, the data from both sites combined for the past four year period exhibited a statistically significant decrease in dioxin levels.

Because of the statistically significant decreases in dioxin levels during the past four years at Site 1, as discussed in the 1990 statistical analysis; and because of the lack of statistically significant increases in dioxin levels at Sites 2 through 5, as discussed in the Final Progress Report and the statistical analysis for the sixth year of the study; and in consideration of the sediment data reported in the Final Progress Report, further sampling and analysis under the Order and Plan is not warranted. In addition to the statistical information, an extension of the program is not called for in light of the extremely low levels of dioxin that have been detected during the course of the seven year study. The discussion of this observation in prior reports to EPA under the Order and Plan is underscored by the fact that the dioxin results obtained in this latest year of the study are the lowest levels ever recorded by the study.

Therefore, in consideration of the statistical analysis and of the extremely low levels of dioxin detected, particularly in this most recent year of the study, Syntex respectfully requests that EPA agree to the termination of the sampling and analysis program under the Order and Plan.

3127Q

STATISTICAL ANALYSIS OF DIOXIN DATA FROM SPRING RIVER

STATISTICAL PACKAGE

REPORT PREPARED BY: Shan-Shan Chen, MPH
Johanna S. Hunt, MStat

BIOSTATISTICIAN: Shan-Shan Chen, MPH

BIOANALYST: Michal Ben-Shachar, M.S.

Institute for Research Data Management
Syntex Research
Palo Alto, California

November 12, 1990

TABLE OF CONTENTS

I. STATISTICAL RESULTS

The dioxin concentrations in fish at the 0.3 mile location downstream from the confluence of the Slough Area and the Spring River were tested for a decrease over time using both a Jonckheere test and a Student's t test. The resulting p-values were 0.15 and 0.07, respectively, showing evidence of a decreasing trend over time. The same tests were conducted on data from site 2 (3.0 miles downstream) resulting in corresponding p-values of 0.43 and 0.26. The results of the two Jonckheere tests yielded a combined p-value of 0.24.

The data from both sites combined were then examined for a decrease over time using multiple linear regression methodology. The 90% confidence interval for the slope over time was (-0.102, 0.004) and the corresponding p-value was 0.06. This analysis also showed strong evidence of a decrease in concentration over the seven sampling years.

The alternative hypothesis tested by the Jonckheere test is that of a monotonic decrease, while the t test detects an overall decreasing trend. The result of the Jonckheere test is more influenced by an apparent increase at any one year, even if it is a function of the assay technique rather than a reflection of a real increase in concentration. In order to examine a more homogeneous set of data, a supplementary

analysis was conducted. All of the above tests were repeated using the data from only the last four years (1987 - 1990). In spite of decreased power due to the smaller sample size, the results indicated a highly significant decrease in dioxin concentrations over the past four years. The only p-value which was not less than 0.05 was that of the Jonckheere test at site 2 ($p = 0.10$). The p-values from the t tests at sites 1 and 2 were 0.007 and 0.03, respectively. The 90% confidence interval for the slope of sampling year was (-0.373, -0.147).

II. STATISTICAL METHODS

General Comments

This report includes the results of statistical analysis of dioxin concentrations in fish sampled at sites 1 and 2 during the years 1984-1990.

All tests were one-sided at a 0.05 significance level. A ninety percent confidence interval for the slope over sampling year was constructed from multiple linear regression. The regression analyses were performed using Release 6.06 of SAS (Statistical Analysis System); and the Jonckheere tests were performed using in-house software written in SAS Version 5.16.

Independent Data Points

One sample was assayed twice. Measurements from the same sample are not independent. To preserve the independence of the data points for statistical analyses, the mean value of the data points measured from the same sample was calculated and assigned to the corresponding sample.

Jonckheere Test

This nonparametric method[1] tested the following ordered alternative at sites 1 and 2:

Ha: C1984 > = C1985 > = C1986 > = C1987 > = C1988 > = C1989 > = C1990

where one of the inequalities must be strict and "Cyear" was the dioxin concentration in a specific year. For each pair of sampling years, this test compared all the possible combinations of two data points from different years and assigned scores as:

1	if Ci > Cj
1/2	if Ci = Cj
0	if Ci < Cj

Since there were two data points in each of the seven sampling years, there were 4 comparisons for each pair of sampling years, and 21 pairs of sampling years. Therefore, the Jonckheere statistic at each site was distributed from 0 to 84. The approximate one-sided alpha-level was calculated using an asymptotic normal distribution method. A corresponding test at each site was conducted on data from the last four years only.

Combined p-Value from Jonckheere Tests

The p-values calculated from Jonckheere tests of data collected at sites 1 and 2 were combined into one p-value using Fisher's method.[2] The chi-squared distribution has the property that (1) a chi-squared statistic having df = d > 1 can be partitioned into several independent chi-squared components, and conversely (2) several independent Chi-squared statistics can be combined into a chi-squared statistic.

The absolute value of twice the natural logarithm of a p-value is distributed as a chi-square with 2 degrees of freedom. Since data from the sites were independent, adding these two chi-squared statistics resulted in a statistic with a chi-squared distribution and 4 degrees of freedom. The corresponding p-value was the combined p-value for the two sites.

Least Squares Linear Regression

The least squares linear regression[3] model was examined using the SAS (Statistical Analysis System) procedure GLM for data collected at sites 1 and 2 separately. The model statement was of the form:

```
MODEL LOGCONC = YEAR
```

where

LOGCONC was the log transformed dioxin concentration, and YEAR was a continuous variable indicating seven (or four) sampling years. From this linear regression analysis, a one-sided t-test was used to test whether the coefficient of sampling YEAR was less than zero (decreasing).

Multiple Linear Regression

The multiple linear regression[3] model was examined using SAS (Statistical Analysis System) procedure GLM for data collected at sites 1 and 2 combined. The model statement was of the form:

```
MODEL LOGCONC = YEAR DISTANCE
```

where

LOGCONC was the log transformed dioxin concentration, YEAR was a continuous variable indicating seven (or four) sampling years, and DISTANCE was a continuous variable indicating the distance from the facility at two sampling locations. From this linear regression analysis, a 90% confidence interval was constructed for the slope over sampling year. This slope was also tested for a decrease using a one-sided t-test.

REFERENCES

1. Hollander, M. and Wolfe, D. (1973). Nonparametric Statistical Methods. John Wiley and Sons.

2. Fisher, R.A. (1958). Statistical Methods for Research Workers. Oliver and Boyd.

3. Draper, N.L. and Smith, H. (1966). Applied Regression Analysis. John Wiley and Sons.

ug/dioxin1990.jsh

III. TABLE

1. Dioxin Concentration (pptr) in Fish

SPRING RIVER, MISSOURI

TABLE 1

DIOXIN CONCENTRATION (pptr) IN FISH

LOCATION (MILES DOWNSTREAM FROM THE FACILITY)	DIOXIN CONCENTRATION (pptr) SAMPLING YEAR 1984	1985	1986	1987	1988	1989	1990	ONE-TAILED P-VALUE* JONCKHEERE TEST	T-TEST
1 (0.3)	4, 4	4.5, 3.0	2.8, 2.5	6.5, 4.8	3.0, 3.2	4.7, 3.3	1.6/1.8, 2.1	0.15 (0.02)	0.07 (0.007)
2 (3.0)	3, 4	3.0, 3.0	2.3, 4.4	4.0, 3.4	4.2, 5.9	3.5, 4.1	1.9, 2.0	0.43 (0.10)	0.26 (0.03)

MULTIPLE LINEAR REGRESSION ANALYSIS OF LOCATIONS 1-2:

* ONE-TAILED P-VALUE FROM T-TEST OF NEGATIVE COEFFICIENT OF SAMPLING YEAR P = 0.06 (<0.01)

* 90% CONFIDENCE INTERVAL FOR THE SLOPE OF SAMPLING YEAR CI = (-0.102,0.004) (CI = (-0.373,-0.147))

COMBINATION OF PROBABILITIES FROM JONCKHEERE TESTS OF SIGNIFICANCE AT LOCATIONS 1-2: P-VALUE = 0.24 (0.01)

NOTE: 1. AT THE SAME SITE AND YEAR, DATA FROM THE SAME SAMPLE ARE SEPARATED BY "/"; DATA FROM INDEPENDENT SAMPLES ARE SEPARATED BY ",".
2. FOR LINEAR REGRESSION ANALYSIS, NATURAL LOG TRANSFORMATION WAS APPLIED TO DIOXIN CONCENTRATION.
3. P-VALUE/CONFIDENCE INTERVAL IN PARENTHESES IS FROM THE CORRESPONDING ANALYSIS OF 4 YEARS OF DATA (1987-1990).

*ONE-TAILED P-VALUE FROM: 1. JONCKHEERE TEST OF DECREASING RANK ORDER OF DIOXIN CONCENTRATION, 2. T-TEST OF NEGATIVE COEFFICIENT FOR SAMPLING YEAR FROM LINEAR REGRESSION ANALYSIS.

SOURCE: IRDM RMBS EPAPLOT (11/5/90 10:56) MBS$1075 #JONCKEPA (11/9/90) SSC$4945 #PROB (11/9/90)
RMBS EPAPLOT2 (11/9/90 9:34)

ug/dioconsampyr.ssc

IV. FIGURES

1. Dioxin Concentration in Fish (Log Transformed Data) - Location 1

2. Dioxin Concentration in Fish (Log Transformed Data) - Location 2

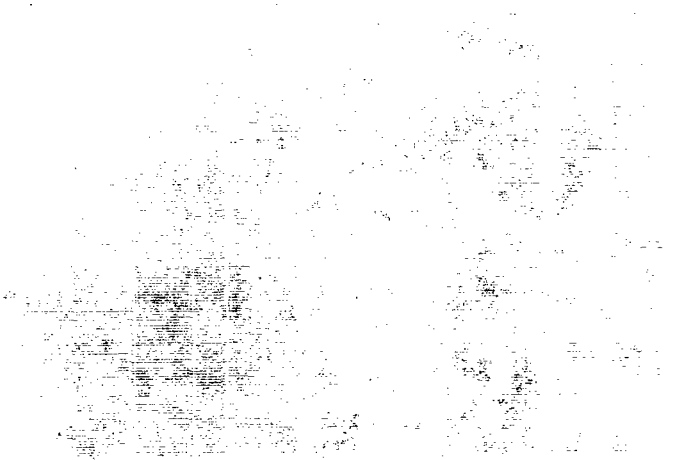
3. Dioxin Concentration in Fish (Raw Data)

4. Residuals of Dioxin Concentration from Linear Regression: Location 1 - Fish Data

5. Residuals of Dioxin Concentration from Linear Regression: Location 2 - Fish Data

6. Dioxin Concentration in Fish (Log Transformed Data) - Locations 1 and 2

7. Residuals of Dioxin Concentration from Multiple Regression: Locations 1 and 2 - Fish Data



MEMO
20 November 1990

To: D. Robertson

From: J. Hunt

Subject: Graphs of Data for 1990 Dioxin Report

Please find attached seven plots of data to be appended to the statistical report sent to you earlier concerning dioxin concentrations in fish samples from the Spring River. You will also find a revised list of figures (page 9). It should replace the list currently included in the statistical report.

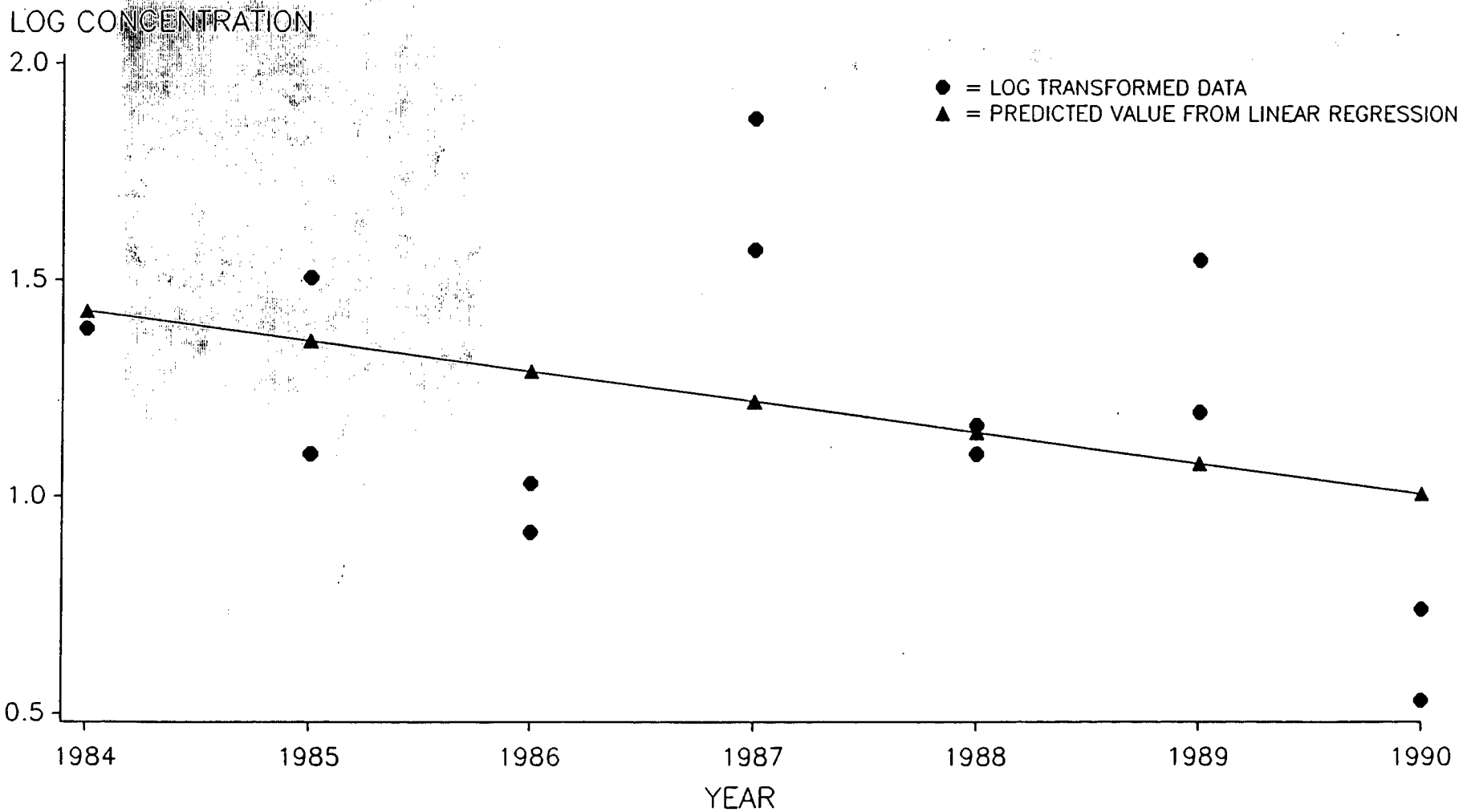
If I can be of any further assistance, please let me know.

SPRING RIVER, MISSOURI

FIGURE 1

DIOXIN CONCENTRATION IN FISH

LOG TRANSFORMED DATA -- LOCATION 1



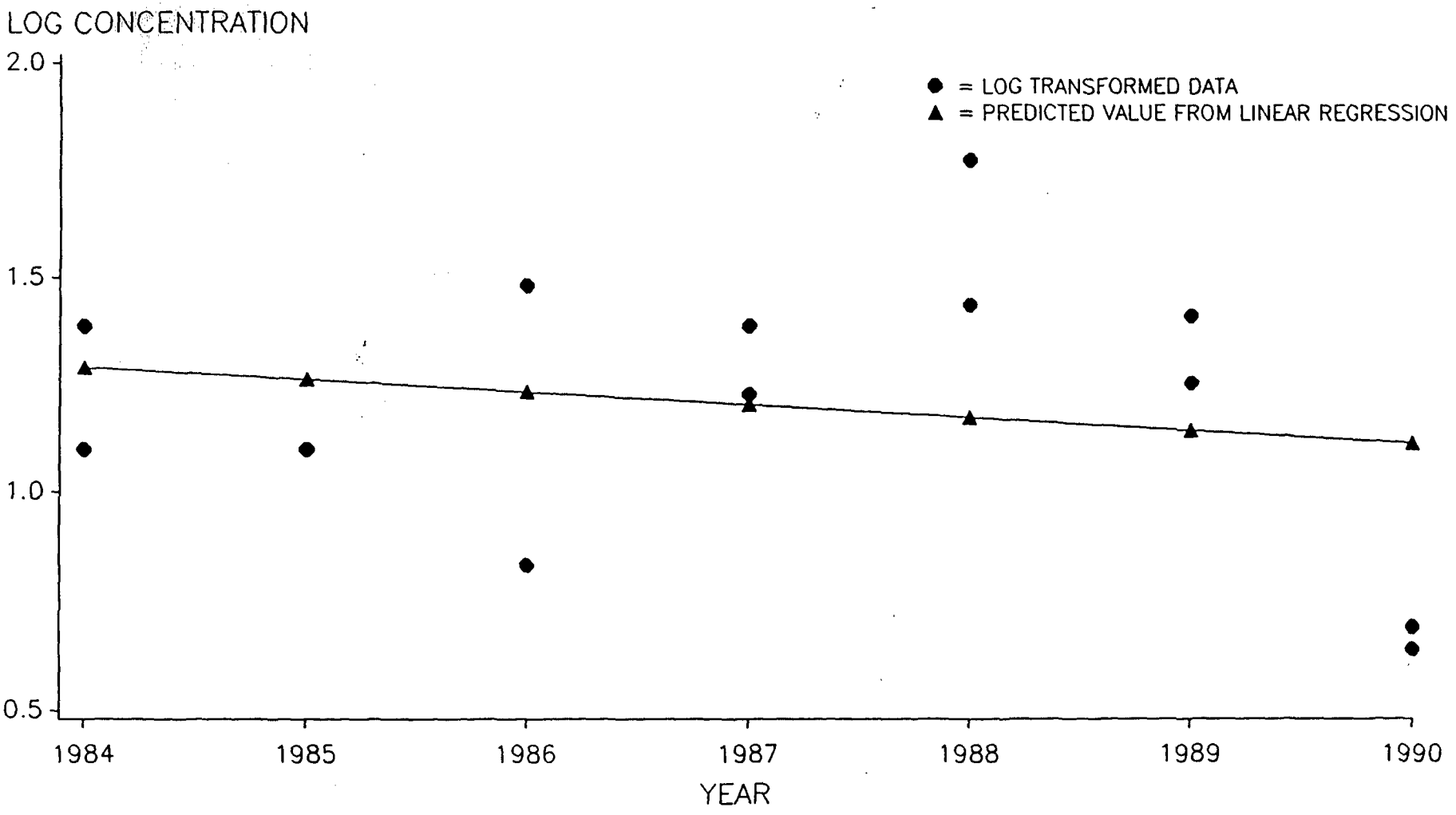
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT1 (19NOV90 08:49)

SPRING RIVER, MISSOURI

FIGURE 2

DIOXIN CONCENTRATION IN FISH

LOG TRANSFORMED DATA -- LOCATION 2

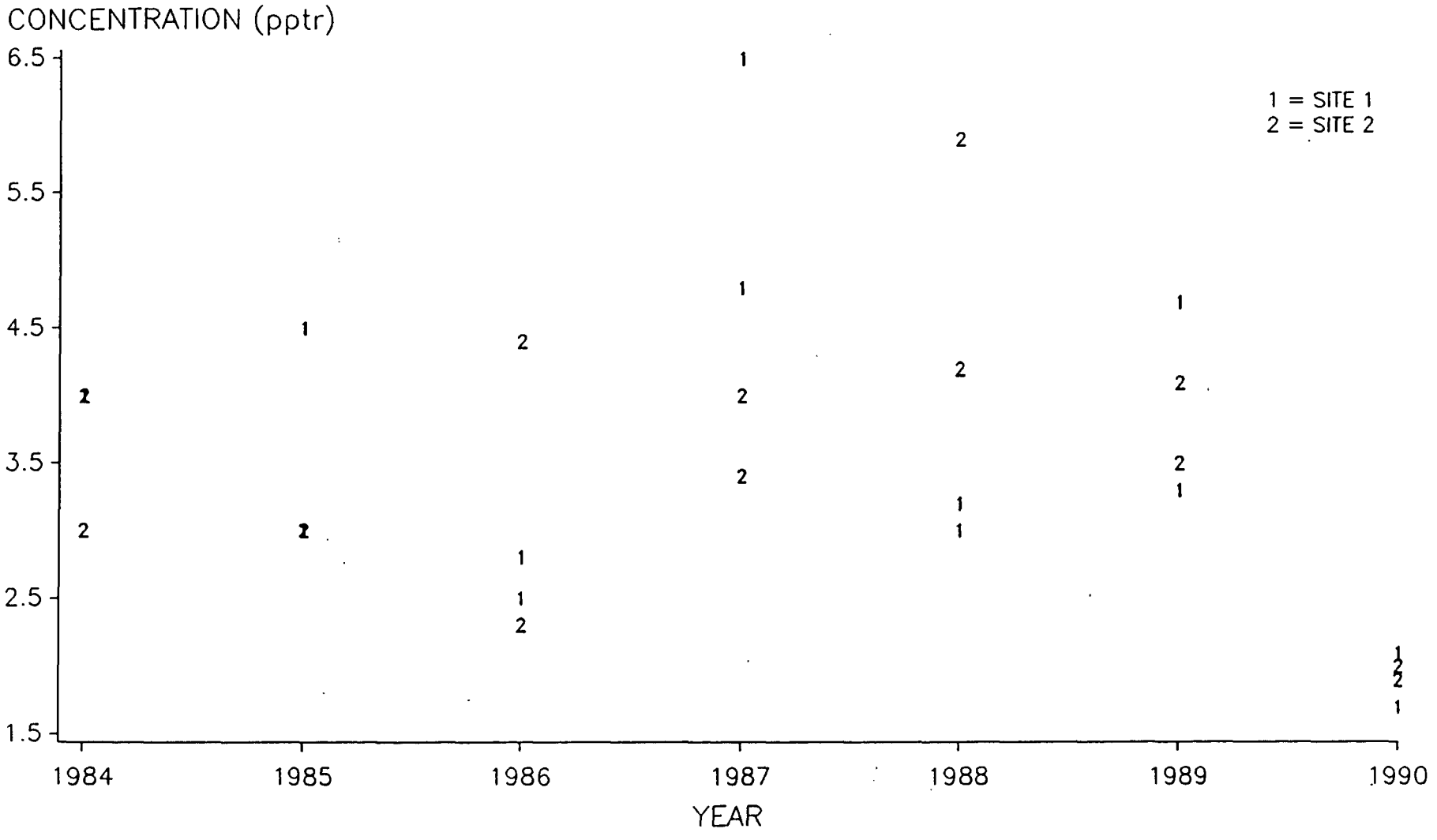


SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT1 (19NOV90 08:49)

SPRING RIVER, MISSOURI

FIGURE 3

DIOXIN CONCENTRATION IN FISH (RAW DATA)



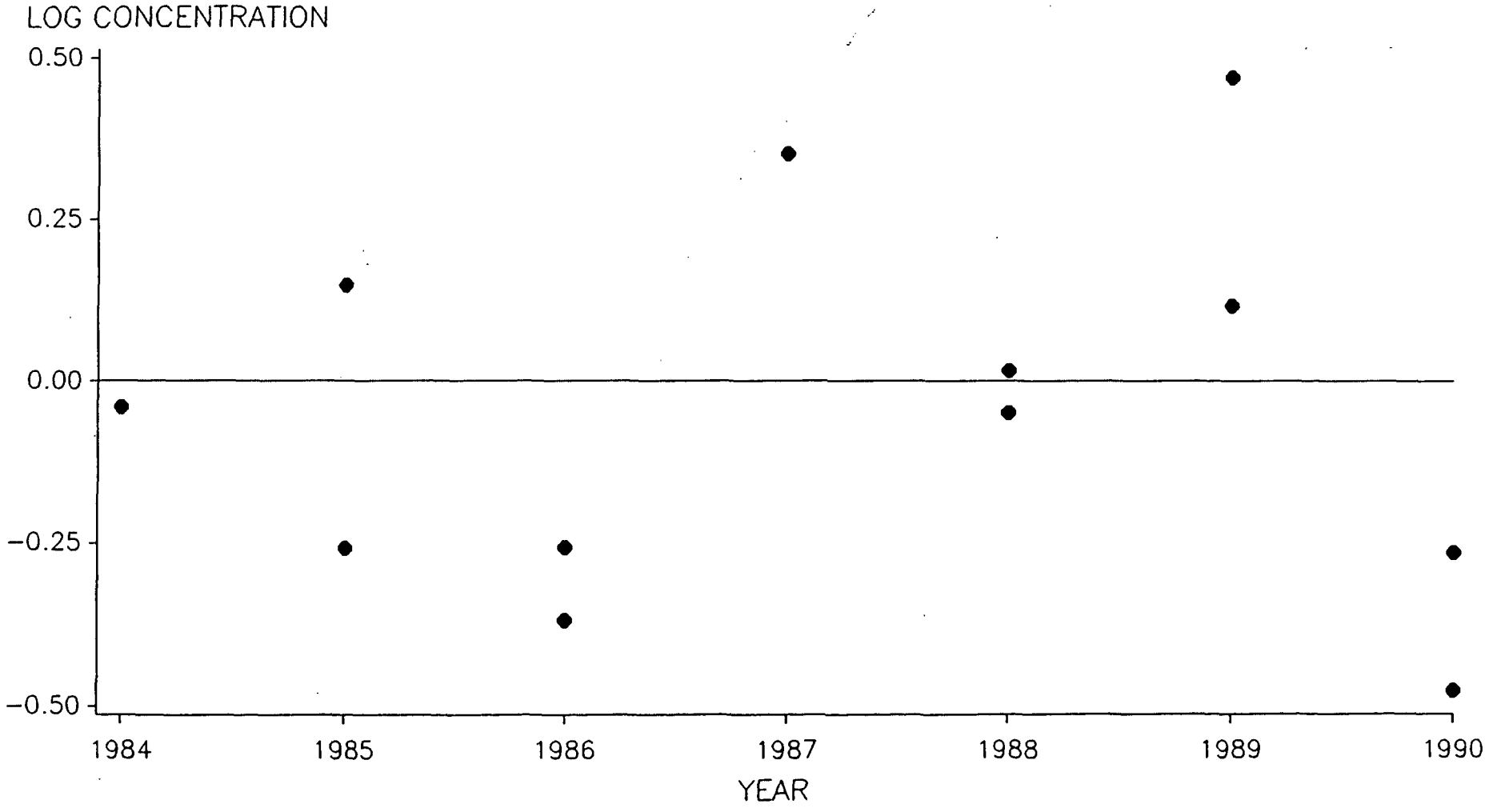
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT3 (19NOV90 08:48)

SPRING RIVER, MISSOURI

FIGURE 4

RESIDUALS OF DIOXIN CONC. FROM LINEAR REGRESSIONS

LOCATION 1 -- FISH DATA



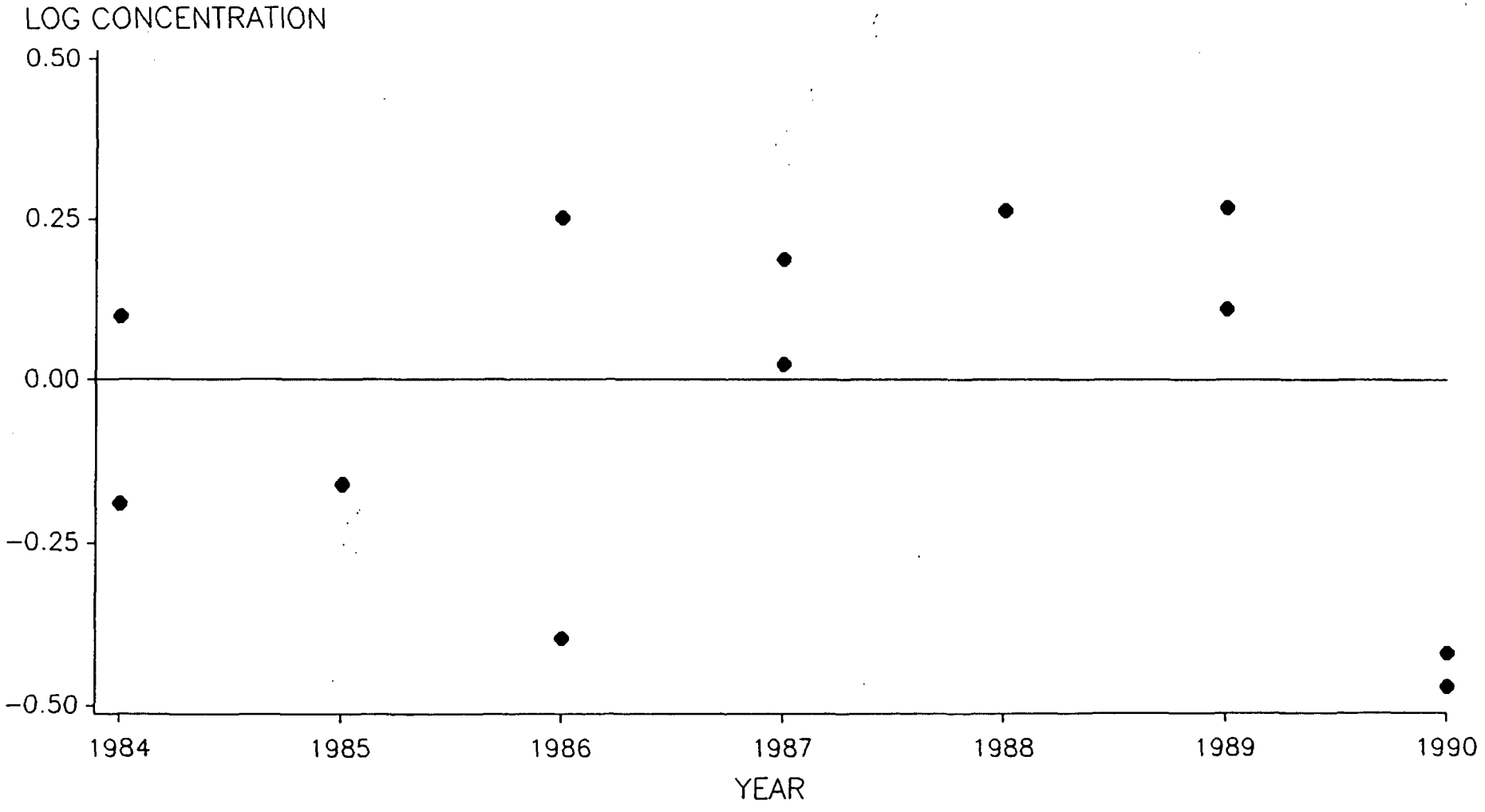
SOURCE: *IRDM RMBS (05NOV90 10:55), RWMC PLOT4 (19NOV90 08:49)*

SPRING RIVER, MISSOURI

FIGURE 5

RESIDUALS OF DIOXIN CONC. FROM LINEAR REGRESSIONS

LOCATION 2 -- FISH DATA



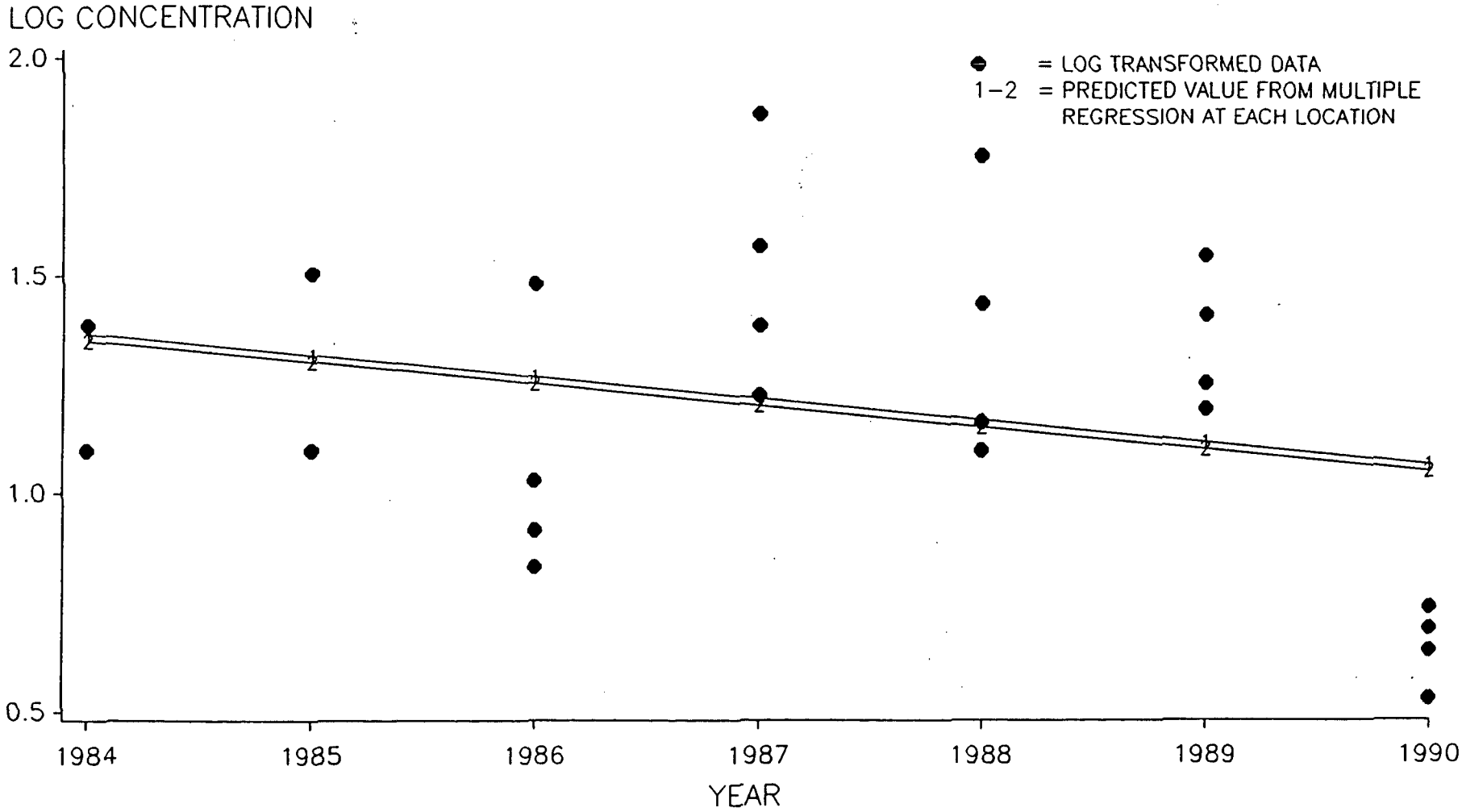
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT4 (19NOV90 08:49)

SPRING RIVER, MISSOURI

FIGURE 6

DIOXIN CONCENTRATION IN FISH

LOG TRANSFORMED DATA -- LOCATIONS 1-2



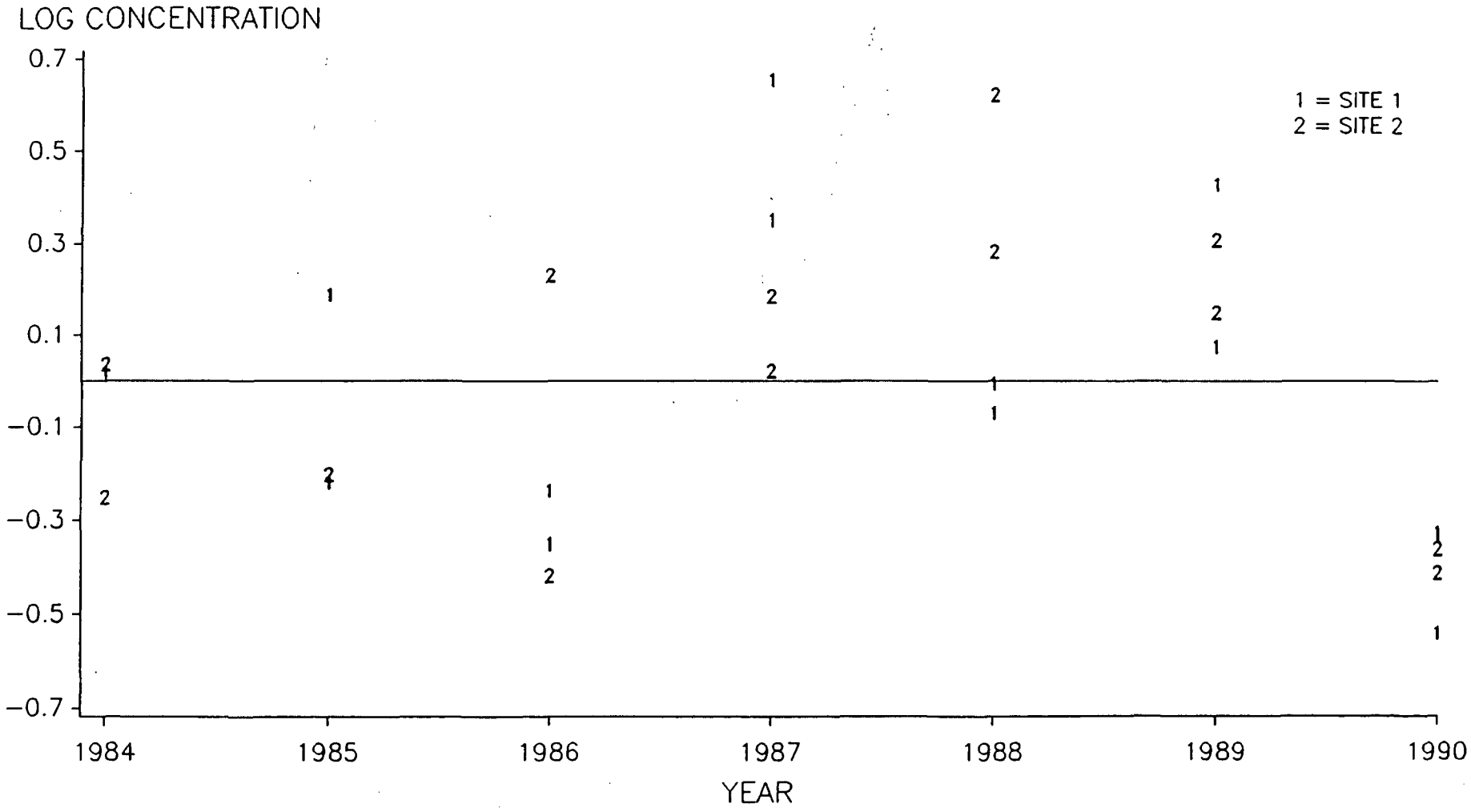
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT6 (19NOV90 10:51)

SPRING RIVER, MISSOURI

FIGURE 7

RESIDUALS OF DIOXIN CONC. FROM MULTIPLE REGRESSION

LOCATIONS 1–2 -- FISH DATA



SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT7 (19NOV90 10:51)

ANALYTICAL AND ENVIRONMENTAL RESEARCH

MEMORANDUM

TO: D. Robertson (w/ attachments) AER: wp0423

FROM: K. Chan
B. Berridge

CC: K. Straub
L. Throop
L. Tokes

DATE: October 3, 1990

SUBJECT: Determination of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (2,3,7,8-TCDD) in Spring River Fish Collected in August, 1990.

This memorandum describes the results of the seventh year study of Verona fish. Levels of 2,3,7,8-TCDD in Catostomus commersoni (white suckers) collected from Verona's Spring River were determined using Syntex Method AR# 10,349 ("Determination of 2,3,7,8-TCDD in Fish by Capillary Gas Chromatography High Resolution Mass Spectrometry Using The Selected Ion Monitoring Technique (C-GC/HRMS-SIM)"). A summary of the results is shown in Table 1.

The fish were collected at only sites 1 and 2 of previous years (1984 - 1989) by the Missouri Department of Conservation (MDC) on August 7, 1990. The exact locations are described in the sampling records (Attachment 1). Subsequently, MDC and Environmental Trace Substances Research Laboratory prepared samples containing homogenate of fish fillets, remainders, and whole fish. Portions of each of these samples were packaged in polyethylene bags and were sent to Syntex for analysis. Syntex (c/o Dr. D. Robertson) received these samples from Ms. Cynthia S. Morris of MDC on September 11, 1990; the samples were frozen and in good condition upon arrival. At Syntex, these samples were stored frozen until just before the preparation for C-GC/HRMS-SIM analysis.

As previously agreed by Syntex and MDC, only the fillets were analyzed in this study. The samples were prepared for analysis by B. Berridge. 1.912 ng of ^{14}C labelled 2,3,7,8-TCDD was added to approximately 50 g of sample. The samples were saponified, extracted, and purified by column chromatography. Finally, the samples were reconstituted in 50 μl of toluene and submitted for C-GC/HRMS-SIM analysis.

These analyses were carried out by K. Chan using a Finnigan-MAT 8230 mass spectrometer directly coupled with a Varian 3700 gas chromatograph. Data were obtained using Finnigan SS300 version 6.01C software. Experimental conditions are shown with the raw data in the attachments. Areas of the chromatographic peaks were obtained and reported using SS300 programs "PAREA" and "PLIST". As in previous years, these data were then inserted to the "TCDD Report Program" (written by B. Brunck, last revision February 11, 1988) which was executed on an IBM PC to perform linear regression analysis on the calibration curves, to calculate the amount of 2,3,7,8-TCDD in the fish samples, and to generate reports as shown in the attachments.

As quality control, a standard addition experiment was carried out. 0.320 ng of 2,3,7,8-TCDD was added to 47.3 g of fillet of group B fish collected at site 2 (sample I.D. MDC90-7S). Analysis of this spiked sample showed a concentration of 8.8 ppt 2,3,7,8-TCDD, which is identical to the expected value (2.0 ppt + 6.8 ppt spike).

The above results show that the concentration of 2,3,7,8-TCDD in the fish samples collected from Spring River this year is slightly lower than the levels detected in 1989.

Attachments: 1. Sampling Records.
2. Documentation of TCDD Standards.
3. Raw data and "TCDD Reports".

TABLE 1

Concentration (in parts per trillion, ppt) of 2,3,7,8-TCDD in Catostomus commersoni Collected From the Verona Spring River in 1990.

Sample I.D.	Site-Group	Type	Results (ppt)
MDC90-1	1-A	Fillet	1.6/1.8[1]
MDC90-2	1-B	Fillet	2.1
MDC90-6	2-A	Fillet	1.9
MDC90-7	2-B	Fillet	2.0

1. Duplicate sample preparation and analysis.

September 7, 1990

Mr. Robert Morby
Region VII
U.S. Environmental Protection Agency
726 Minnesota Avenue
Kansas City, Kansas 55101

Dear Mr. Morby:

On August 7, 1990 white suckers (Catostomus commersoni) were collected from two locations on the upper Spring River for TCDD analysis. This is in compliance with the seventh year of a continuing requirement outlined in the revised Verona Fish and Sediment Sampling Plan. The fish were collected by electroshocking and a representative from Syntex was present during sampling. The two sites correspond to those identified in the "Verona Plant, Fish and Sediment Plan". Site 5 was dropped in 1989 and sites 3 and 4 were dropped in 1990. These sites were identical to those sampled in August of 1984, 1985, 1986, 1987, 1988 and 1989. The sampling locations are identified in Attachment A. The size and weight of each fish and the identifying number is listed in Attachment B. The recommended minimum numbers of fish were met at all locations.

The fish were taken to our facility at Columbia, Missouri, thawed and prepared accordingly. The fish at site 2 were weighed and measured and sequentially placed into two equal size groups designated as Groups A and B. The right skinless fillets of the fish in Groups A and B were removed and placed in separate polyethylene bags. These two groups are to be analyzed separately. The remainder of Group B fish (the entire fish minus the right fillet) was placed in a third bag for analysis. A fourth whole body estimate will be calculated. The fish at Site 1 were prepared in a similar manner except they were sorted into three equal size groups. Group A and B were prepared in a manner identical to site 2 and the fish in Group C were simply left whole and refrozen. Thus a total of seven composites were prepared which will generate nine measurements (two calculated).

The frozen fish samples were delivered to the Environmental Trace Substances Research Laboratory in Columbia, thoroughly homogenized, a maximum of 100-gram samples were removed, refrozen, and delivered to Dr. David Robertson, Syntex Research, Palo Alto, California by Federal Express on September 10, 1990.

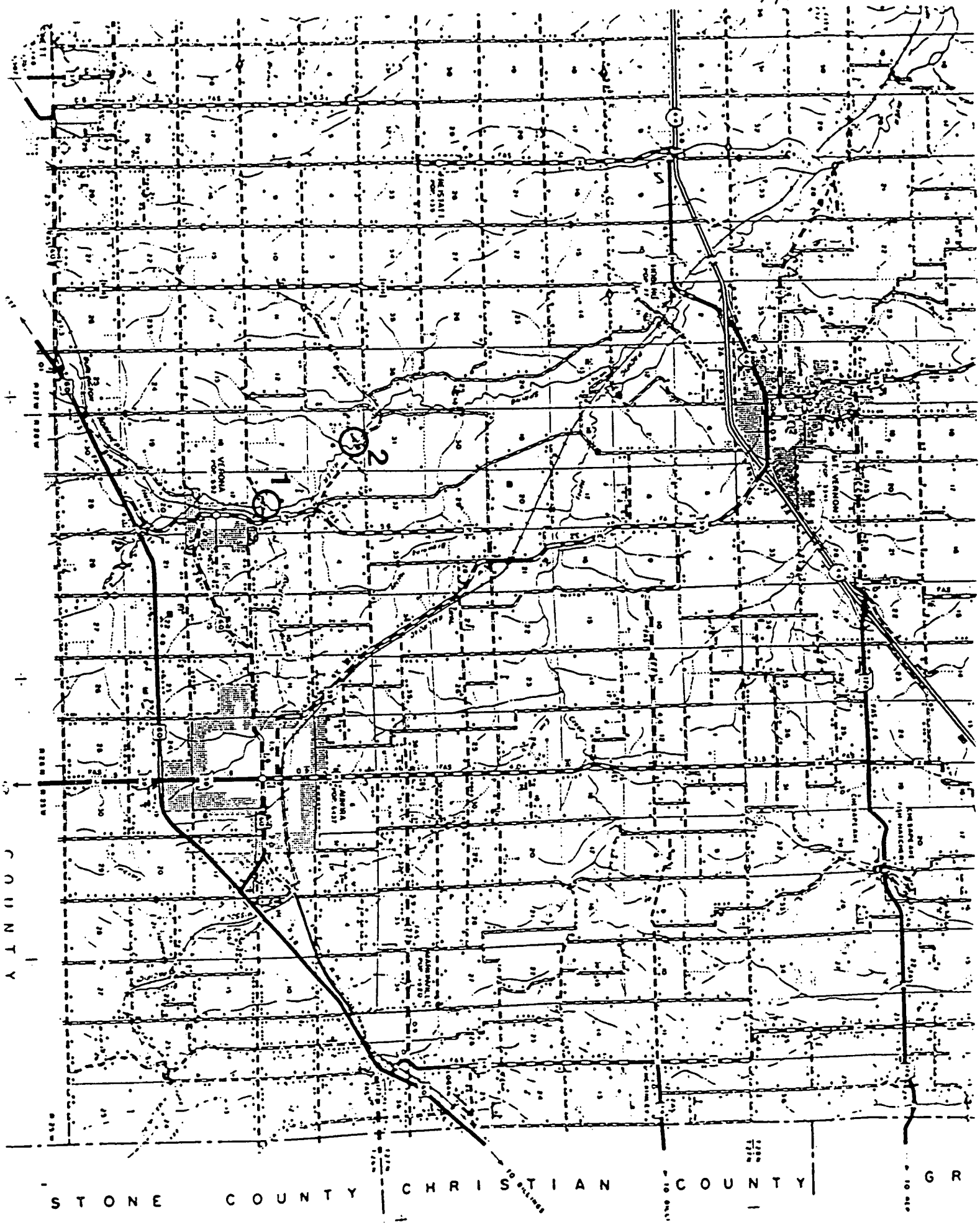
Sincerely,

Cynthia S. Morris
Fisheries Environmental Specialist

Enclosure

bcc: Stan Michaelson Alan Buchanan Glen Curtis
Steve Weithman David Robertson

A1-2



Attachment B

Site 1 - Group A - Fillets Only

Total Length (mm)	Weight (kg)	MDC Number
340	.420	MDC90-1 90ENV007
308	.300	
277	.210	
240	.138	

Site 1 - Group B - Fillets and Remainder

Total Length (mm)	Weight (kg)	MDC Number
328	.371	MDC90-2 (fillets) 90ENV008
297	.271	and
250	.167	MDC90-3 (remainder) 90ENV009
238	.147	and MDC90-4* (to be calculated)

Site 1 - Group C - Whole Fish

Total Length (mm)	Weight (kg)	MDC Number
330	.268	MDC90-5 90ENV010
305	.285	
339	.136	
243	.138	

Site 2 - Group A - Fillets Only

Total Length (mm)	Weight (kg)	MDC Number
325	.367	MDC90-6 90ENV011
302	.300	
310	.300	
244	.138	

Site 2 - Group B - Fillets and Remainder

Total Length (mm)	Weight (kg)	MDC Number
315	.332	MDC90-7 (fillets) 90ENV012
320	.381	and
247	.152	MDC90-8 (remainder) 90ENV013
226	.112	and MDC90-9* (to be calculated)

* Total weight of fillets for Group 1B fish is .182 kg for calculation purposes.

* Total weight of fillets for Group 2B fish is .170 kg for calculation purposes.

Read and Understood by _____ Date _____

Preparation and Analysis

Samples of the unlabeled 2,3,7,8-TCDD and ^{13}C-2,3,7,8-TCDD used in the preparation of SRM 1614 were donated by R. Mitchum, National Center for Toxicological Research, Jefferson AK. The unlabeled 2,3,7,8-TCDD was originally obtained from ECO Control, Inc., Cambridge, MA; and the ^{13}C-labeled 2,3,7,8-TCDD from Midwest Research Institute, Kansas City, MO. The purities of the labeled and unlabeled 2,3,7,8-TCDD used in the preparation of this SRM were determined at NBS using mass spectrometry, nuclear magnetic resonance spectrometry, and GC with flame ionization detection. The purities were found to be greater than 95%.

Solutions of the unlabeled 2,3,7,8-TCDD and the ^{13}C-labeled 2,3,7,8-TCDD were prepared at NBS by weighing and mixing the appropriate compound and isooctane. Each solution was dispensed into 2-mL amber ampoules which were then flame sealed. Aliquots from randomly selected ampoules were analyzed with a gas chromatograph equipped for split injection and a 30m x 0.25mm i.d. wall-coated open-tubular column with a 0.25 μm film of a non-polar, immobilized phase. A constant current electron capture detector (^{63}Ni) was used for these analyses. Quantitative results were obtained through the use of 2,2',4,4',5,5'-hexachlorobiphenyl as an internal standard. Calibration solutions consisting of weighed amounts of the analyte and the internal standard compound in isooctane were analyzed chromatographically to determine response factors.

A trichlorodibenzo-p-dioxin impurity present in both solutions was quantified using GC/MS with electron impact ionization, selected ion monitoring, and the method of standard additions. Standard additions of unlabeled 2,3,7-trichlorodibenzo-p-dioxin were made to the unlabeled and ^{13}C-labeled 2,3,7,8-TCDD solutions, and although the retention time of the trichlorodibenzo-p-dioxin impurity was coincident with that of the 2,3,7-isomer, this was not sufficient to positively identify which isomer was present. Concentrations of the trichlorodibenzo-p-dioxin in the SRM solutions are provided, for information only, in Table 2.

Expiration of Certification

This certification is valid within the specified limit of uncertainty for one year from the date of purchase. In the event that the certification should become invalid before then, purchasers will be notified by NBS.

Storage

Sealed ampoules, as received, should be stored in the dark at temperatures between 10 and 30 °C. It is recommended that these materials be stored in a secure area in a double-sealed container.

Use

Samples of the SRM should be withdrawn from ampoules (at 23 ± 8 °C) immediately after opening and used without delay for the certified values listed in Table 1 to be valid within the stated uncertainties. Certified values are not applicable to material in ampoules stored after opening, even if they are resealed.

Preparation and analytical determinations were performed in the NBS Organic Analytical Research Division by S.N. Chesler, B. Coxon, L.R. Hilpert, R.M. Parris, R.E. Rebbert, M.J. Welch, and E. White. V.

Consultation on the statistical design of the experimental work and evaluation of the data was provided by R.C. Paule of the NBS National Measurement Laboratory.

The coordination of the technical measurements leading to the certification of SRM 1614 was under the direction of L.R. Hilpert, R.M. Parris, and W.E. May.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by T.E. Gills.

continued
next page

8/21/87

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1614

Dioxin (2,3,7,8-TCDD in Isooctane)

Standard Reference Material (SRM) 1614 consists of separate solutions of unlabeled and labeled 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in 2,2,4-trimethylpentane (isooctane). Three ampoules contain approximately 1.2 mL each of an isooctane solution of unlabeled 2,3,7,8-TCDD, and three ampoules contain approximately 1.2 mL each of an isooctane solution of ^{13}C-labeled 2,3,7,8-TCDD. This SRM is intended primarily for use in the evaluation of analytical methods used in the determination of 2,3,7,8-TCDD. It can also be used to fortify samples with known amounts of 2,3,7,8-TCDD. The ^{13}C-labeled 2,3,7,8-TCDD can be used as an internal standard in methods based on gas chromatography/mass spectrometry (GC/MS).

Certified Concentrations of 2,3,7,8-TCDD

The certified concentrations and estimated uncertainties of the unlabeled and ^{13}C-labeled 2,3,7,8-TCDD solutions are given in Table 1. The concentration values are certified in ng/g units, but are also reported in ng/mL units for user convenience. The ^{13}C-labeled solution is certified for the total concentration of all isotopic forms of 2,3,7,8-TCDD. The isotopic purity of the ^{13}C-labeled material was determined to be 98.2 ± 0.1 atom percent ^{13}C by mass spectrometry. The fully ^{13}C-labeled compound, 2,3,7,8-TCDD-$^{13}C_{12}$, accounts for 80.7 ± 0.5 percent of the 2,3,7,8-TCDD molecules in the sample.

The certified values are the weighted averages of gravimetric values, based on the concentration calculated from the mass of 2,3,7,8-TCDD added to a known mass of isooctane and on the analytical results obtained using capillary gas chromatography with electron capture detection (GC/ECD). The uncertainties are two standard deviations of the certified values. These uncertainties include the gravimetric and GC measurement variability and any observed material heterogeneity.

NOTICE AND WARNING TO USERS

Handling

The toxicity and/or carcinogenicity of 2,3,7,8-TCDD has not been precisely defined; however, this material should be treated as a potential health hazard. Ampoules should be opened and the contents used only by persons trained in proper handling techniques. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD. Users in the United States should contact their regional offices of the U.S. Environmental Protection Agency for information regarding proper disposal of these materials; in other countries, they should contact the appropriate organization responsible for public health or environmental control.

Trimethylpentane (isooctane), used as a diluent in this SRM, is stable when stored in closed containers at room temperature. It will not undergo hazardous polymerization. However, it is highly flammable and should be kept away from oxidizing agents.

Gaithersburg, MD 20899
July 8, 1985

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

National Bureau of Standards Certificate of Analysis for Standard Reference Material 1614

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A2-2

National Bureau of Standards Certificate of Analysis for Standard Reference Material 1614

— continued from p. 82

Table 1

Certified Concentrations of 2,3,7,8-TCDD[a] in SRM 1614

Compound	Concentration[b] ng/g	Concentration[b] ng/mL[c], 23 °C
2,3,7,8-TCDD	98.3 ± 3.3	67.8 ± 2.3
2,3,7,8-TCDD-^{13}C[d]	95.6 ± 1.5	65.9 ± 1.0

[a] CAS Registry Numbers: 2,3,7,8-TCDD-$^{12}C_{12}$: 1746-01-6; 2,3,7,8-TCDD-$^{13}C_{12}$: 76523-40-5, Chemical Abstracts, Tenth Collective Index, Index Guide, American Chemical Society, Columbus, Ohio, 1982.

[b] The uncertainties given represent two standard deviations of the certified values. These uncertainties include the gravimetric and GC/ECD 2,3,7,8-TCDD measurement variability, the trichlorodibenzo-p-dioxin measurement variability, and, for the unlabeled 2,3,7,8-TCDD, the observed sample heterogeneity.

[c] The concentration and uncertainty expressed in mass/volume units are applicable for use of this material at 23.0 °C. Since the density of 2,2,4-trimethylpentane changes with temperature, the concentration will change at temperatures other than 23.0 °C. The concentration will change by less than 1 percent of the value listed if the SRM is used at temperatures in the 15 to 31 °C range.

[d] The concentrations given represent the total concentrations for all isotopic forms of 2,3,7,8-TCDD in the solution. The fully ^{13}C-labeled 2,3,7,8-TCDD accounts for 80.7 ± 0.5 percent of the 2,3,7,8-TCDD molecules in the sample. This value is provided for information only.

Table 2

Concentrations of Trichlorodibenzo-p-dioxin in SRM 1614

Solution	Compound	Concentration[a] ng/g	Concentration[a] ng/mL, 23 °C
Unlabeled	trichlorodibenzo-p-dioxin-$^{12}C_{12}$	(1.5)	(1.0)
Labeled (^{13}C)	trichlorodibenzo-p-dioxin-$^{13}C_{12}$	(3.9)	(2.7)

[a] Values not certified; provided for information only.

B. Berridge 8/27/81

Read and Understood by _____ Date _____

A2-3

9/21/90

Preparation of Stock Solutions for Fish Standards and Spiking Solutions

13C-TCDD

DDR-10179-8b was opened and diluted to mark with acetone (nominal ~~10 ng/100 µl~~ 5.606 ng/100 µl Verified Amount)

diluted 1 ml of above to 10 ml with (toluene : acetone = 1:9) to give (10179-143-1)
(nominal 10 ng/100 µl)
9.6606 ng/100 µl Verified Amount

diluted 2 ml of (143-1) to 10 ml with (toluene : acetone = 1:9) to give (10179-143-2)
(nominal ~~2 ng/100 µl~~)
1.9121 ng/100 µl Verified Amount

NATIVE-TCDD

RAB-9002-125 (nominal 31.48 ng/100 µl)

diluted 1 ml of (-125) to 10 ml with (toluene : acetone = 1:9) to give (10179-143-A)
(nominal ~~3.148 ng/100 µl~~)
3.2015 ng/100 µl Verified Amount

diluted 1 ml of (143-A) to 10 ml with (toluene : acetone = 1:9) to give (10179-143-B)
(nominal ~~0.3148 ng/100 µl~~)
0.3202 ng/100 µl Verified Amount

diluted 1 ml of (143-B) to 10 ml with (toluene : acetone = 1:9) to give (10179-143-C)
(nominal ~~0.03148 ng/100 µl~~)
0.0320 ng/100 µl Verified Amount

Read and Understood by _____ Date _____

Preparation of Verification Mixtures

9/21/90

Opened fresh set of vials of NBS Reference Material 1614 see pages 129, 130 of this notebook for documentation.

VERIFICATION MIXTURE	1a	100 µl (6.78 ng) native TCDD Cert. Std. / 100 µl ^{13}C-TCDD (10179-143-1)
" "	1b	
VERIFICATION MIXTURE	2a	200 µl native TCDD (10179-143-A) / 100 µl (5.32 ng) ^{13}C-TCDD Cert. Std.
" "	2b	
VERIFICATION MIXTURE	3a	200 µl native TCDD (10179-143-A) / 100 µl ^{13}C-TCDD (10179-143-1)
" "	3b	

Note: The above material was freshly opened vials of NBS Reference Material 1614. Copies of the documentation appears on pages 82 and 83 of the notebook. One unopened set of vials remain.

Read and Understood by _____ Date _____

VERIFICATION MIXTURE

1a $\frac{\text{native}}{^{13}\text{C-TCDD}} = \frac{180644}{254967} = 0.7085$

1b $\frac{279904}{411918} = 0.6795$ } 0.6940

2a $\frac{241820}{208216} = 1.1614$

2b $\frac{215435}{180396} = 1.1942$ } 1.1778

3a $\frac{272612}{410037} = 0.6648$

3b $\frac{160238}{248079} = 0.6459$ } 0.6554

VER. MIX 3 ÷ VER. MIX 1 = 0.6554 ÷ 0.6940 = 0.9444

$$\frac{200\,\mu l \text{ native TCDD (10179-143-A)}}{100\,\mu l\ ^{13}\text{C-TCDD (10179-143-1)}} \times \frac{100\,\mu l\ ^{13}\text{C-TCDD (10179-143-1)}}{100\,\mu l\ (6.78\,ng) \text{ native TCDD Cert. Std}} = 0.9444$$

200 µl native TCDD (10179-143-A) = 6.4030 ng

native TCDD (10179-143-A = 3.2015 ng/100 µl Verified Amount

VER. MIX 2 ÷ VER. MIX 3 = 1.1778 ÷ 0.6554 = 1.7971

$$\frac{200\,\mu l \text{ native TCDD (143-A)}}{100\,\mu l\ (5.32\,ng)\ ^{13}\text{C-TCDD Cert. Std.}} \times \frac{100\,\mu l\ ^{13}\text{C-TCDD (143-1)}}{200\,\mu l \text{ native TCDD (143-A)}} = 1.7971$$

^{13}C-TCDD (10179-143-1) = 9.5606 ng/100 µl Verified Amount

Chromatograms appear on pages 147-152 of this notebook.

Read and Understood by _____ Date _____

Preparation of Standards for Fuel Samples 9/21/90

These standards were prepared using the stock solutions prepared and verified, as shown on pages 143 to 145.

Label	Vol. Native TCDD (10179-___)	Vol ^{13}C-TCDD (10179-143-2)	Verified amounts: native/^{13}C-TCDD	Final Volume
2.0	0	100µl	0/1.912 ng	50µl
2.1	50µl (-143-C)	100µl	.016/1.912	50µl
2.2	100µl (-143-C)	100µl	.032/1.912	50µl
2.3	200µl (-143-C)	100µl	.064/1.912	50µl
2.4	50µl (-143-B)	100µl	.160/1.912	50µl
2.5	100µl (-143-B)	100µl	.320/1.912	50µl
2.6	200µl (-143-B)	100µl	.640/1.912	50µl
2.7	50µl (-143-A)	100µl	1.601/1.912	50µl
2.8	100µl (-143-A)	100µl	3.202/1.912	50µl
2.9	200µl (-143-A)	100µl	6.403/1.912	50µl

B. Berridge 9/25/90

Read and Understood by_____ Date_____

[redacted]

A2-7

$\frac{\text{native TCDD}}{^{13}C\text{-TCDD}} =$

$\frac{\Sigma\ M/E\ 320+322}{\Sigma\ M/E\ 332+334} =$

$\frac{180644}{254967} = 0.7085$

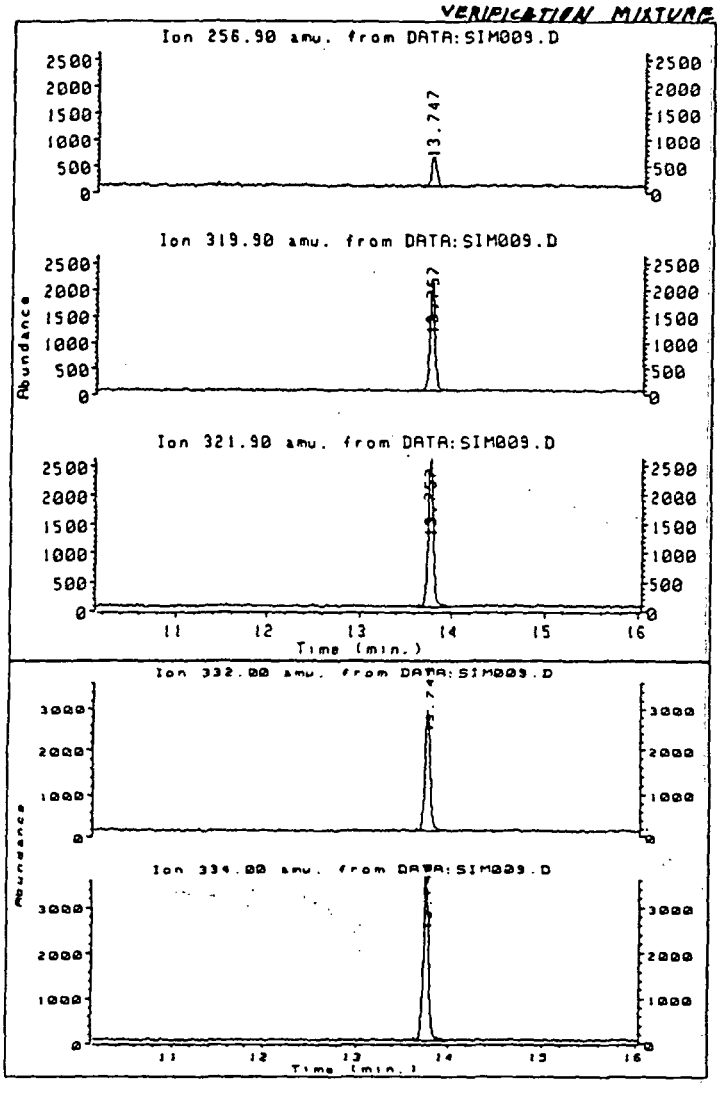
*** Area Percent ***

Report by Retention Time

Operator: B. BERRIDGE 25 Sep 90 6:22 am
Method File Name : SIMTCDD.M
Sample Info : Verification mixture 1a 9/25/90
Misc Info: DATA:SIM009.D
Integration File Name : RESULTS.I
Bottle Number : 0

Ret Time	Signal Descr		Type	Area	Height	% Pk	% Sg	% LPk	% LSg
13.746	Mass	334.00 amu	VV	143614	3562	31.31	100.00	100.00	100.00
13.745	Mass	332.00 amu	PV	111353	2832	24.27	100.00	77.54	100.00
13.757	Mass	321.90 amu	VV	103630	2546	22.59	100.00	72.16	100.00
13.757	Mass	319.90 amu	VV	77014	2035	16.79	100.00	53.63	100.00
13.747	Mass	256.90 amu	VV	23124	559	5.04	100.00	16.10	100.00

VERIFICATION MIXTURE 1a



Read and Understood by_____ Date_____

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native TCDD =
^{13}C-TCDD

279904 = 0.6795
411918

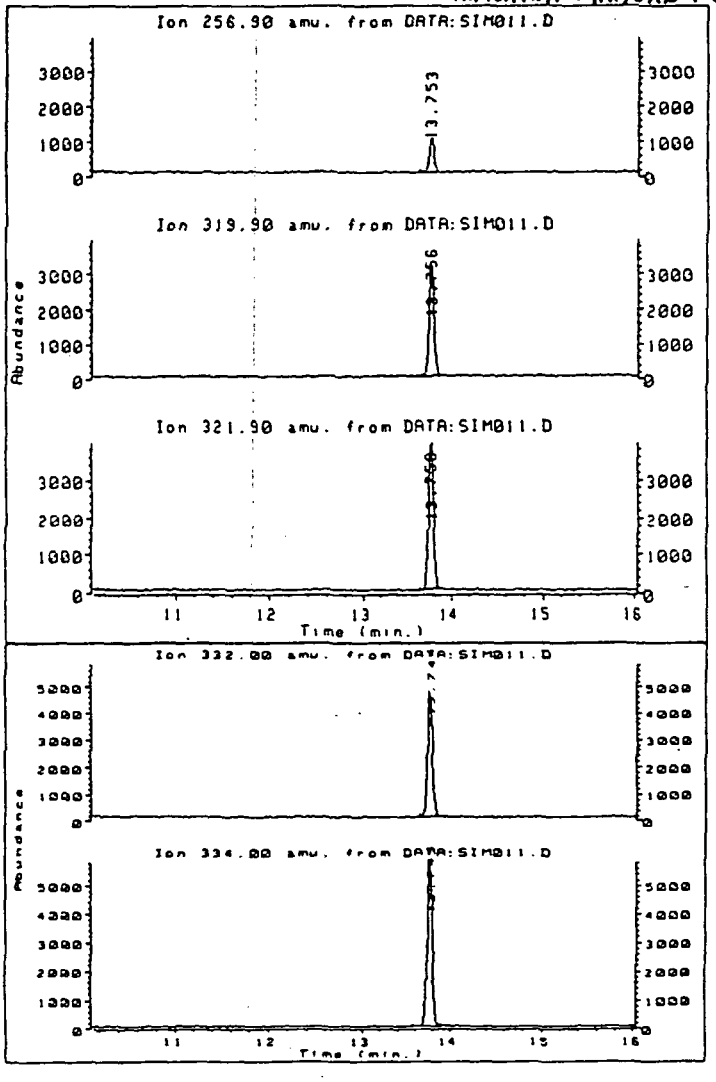
*** Area Percent ***

Report by Retention Time

Operator: B. BERRIDGE 25 Sep 90 8:22 am
Method File Name : SIMTCDD.M
Sample Info : Verification mixture 1b 9/25/90
Misc Info: DATA:SIM011.D
Integration File Name : RESULTS.I
Bottle Number : 0

Ret Time	Signal Descr	Type	Area	Height	% Pk	% Sg	% LPk	% LSg
13.745	Mass 334.00 amu	PV	228025	5749	31.29	100.00	100.00	100.00
13.744	Mass 332.00 amu	PV	183893	4736	25.24	100.00	80.65	100.00
13.756	Mass 321.90 amu	BV	156001	3889	21.41	100.00	68.41	100.00
13.756	Mass 319.90 amu	BV	123903	3142	17.00	100.00	54.34	100.00
13.753	Mass 256.90 amu	BV	36846	959	5.06	100.00	16.16	100.00

VERIFICATION MIXTURE 1b



Read and Understood by _____

1.8.3.

A2-9

*** Area Percent ***

Report by Retention Time

25 Sep 90 9:54 am

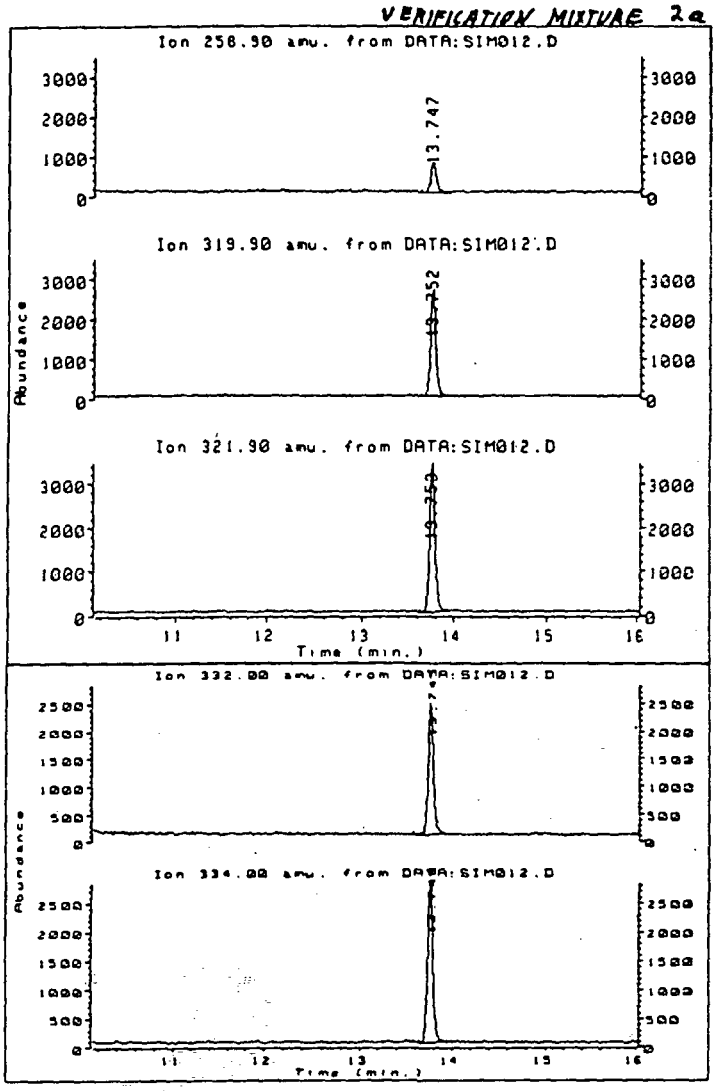
Operator: B. BERRIDGE
Method File Name : SIMTCDD.M
Sample Info : Verification mixture 2a 9/25/90
Misc Info: DATA:SIM012.D
Integration File Name : RESULTS.I
Bottle Number : 0

Ret Time	Signal	Descr	Type	Area	Height	% Pk	% Sp	% LPk	% LSp
13.746	Mass	334.00 amu	VV	113787	2767	23.58	100.00	84.17	100.00
13.745	Mass	332.00 amu	PV	94428	2377	19.57	100.00	69.85	100.00
13.753	Mass	321.90 amu	BV	135188	3328	28.01	100.00	100.00	100.00
13.752	Mass	319.90 amu	PV	106632	2600	22.10	100.00	78.88	100.00
13.747	Mass	256.90 amu	VV	32538	741	6.74	100.00	24.07	100.00

native TCDD
^{13}C-TCDD

241820 / 208216 = 1.1614

VERIFICATION MIXTURE 2a



Read and Understood by_____ Date_____

A2-10

native TCDD =
^{13}C-TCDD

215435 = 1.1942
180396

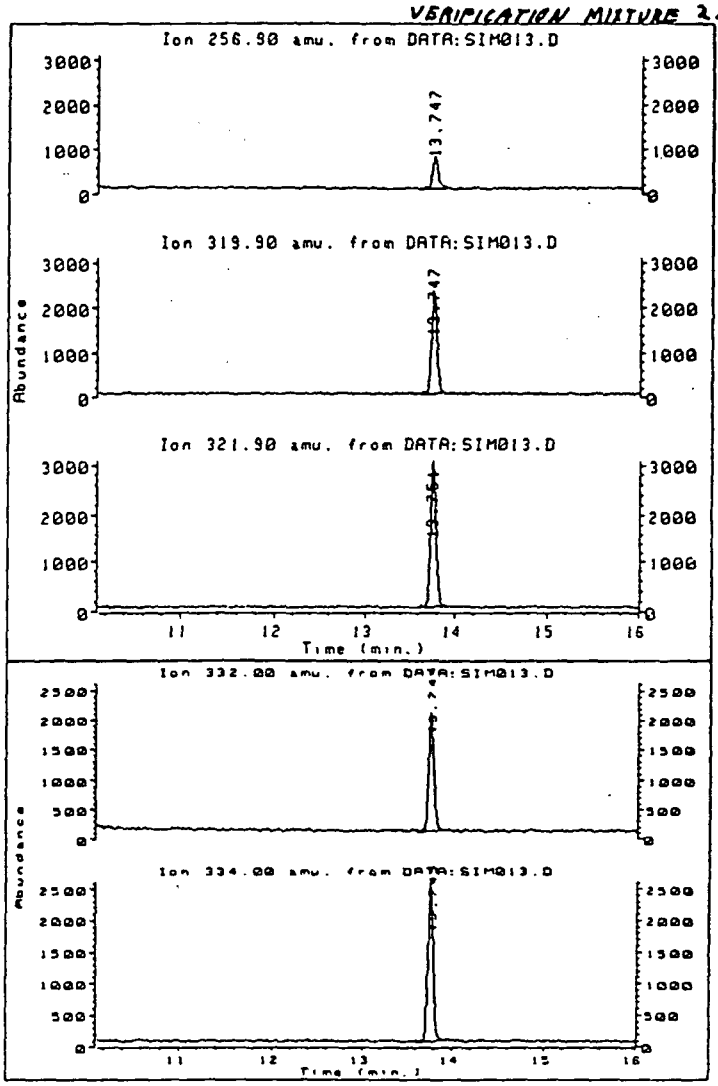
*** Area Percent ***

Report by Retention Time

Operator: B. BERRIDGE 25 Sep 90 10:31 am
Method File Name : SIMTCDD.M
Sample Info : Verification mixture 2b 9/25/90
Misc Info: DATA:SIM013.D
Integration File Name : RESULTS.I
Bottle Number : 0

Ret Time	Signal Descr		Type	Area	Height	% Pk	% Sg	% LPk	% LSg
13.745	Mass	334.00 amu	PV	99843	2584	23.42	100.00	81.62	100.00
13.744	Mass	332.00 amu	PV	80553	1973	18.90	100.00	65.85	100.00
13.751	Mass	321.90 amu	BV	122328	2973	28.70	100.00	100.00	100.00
13.747	Mass	319.90 amu	PV	93107	2337	21.84	100.00	76.11	100.00
13.747	Mass	256.90 amu	VV	30396	748	7.13	100.00	24.85	100.00

VERIFICATION MIXTURE 2b



Read and Understood by _____ Date _____

A2-11

*** Area Percent ***

Report by Retention Time

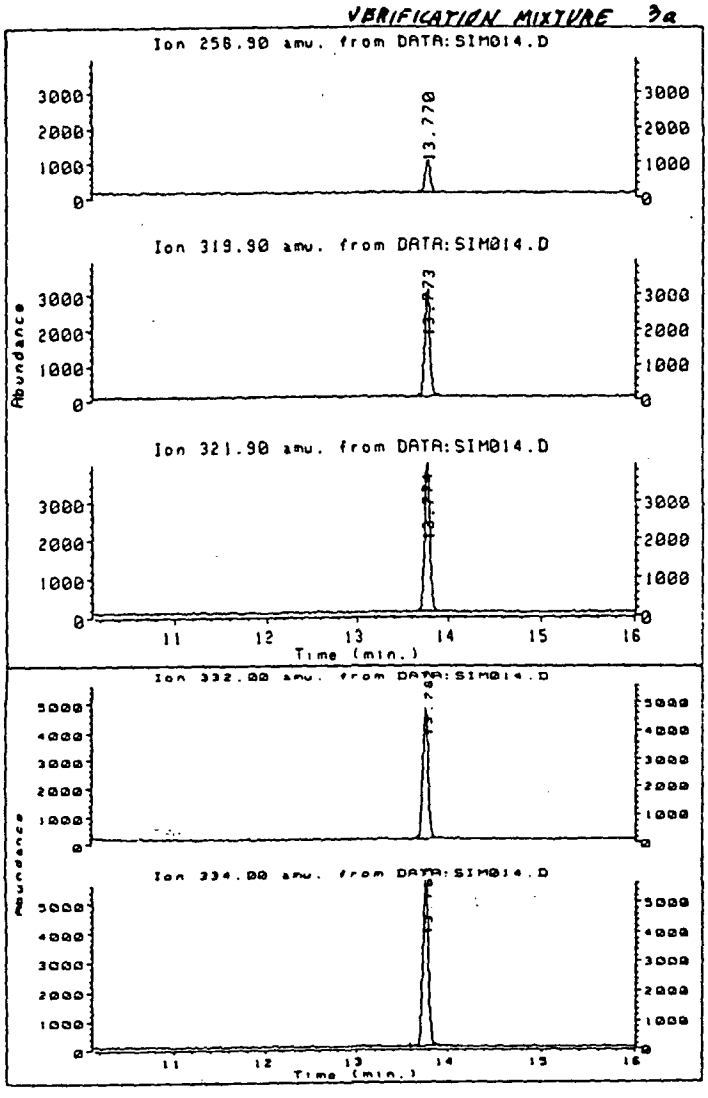
Operator: B. BERRIDGE 25 Sep 90 12:42 pm
Method File Name : SIMTCDD.M
Sample Info : Verification mixture 3a 9/25/90
Misc Info: DATA:SIM014.D
Integration File Name : RESULTS.I
Bottle Number : 0

Ret Time	Signal	Descr	Type	Area	Height	% Pk	% Sg	% LPk	% LSg
13.763	Mass	334.00 amu	PV	226807	5579	31.56	100.00	100.00	100.00
13.762	Mass	332.00 amu	PV	183230	4670	25.49	100.00	80.73	100.00
13.774	Mass	321.90 amu	BV	153337	3891	21.33	100.00	67.61	100.00
13.773	Mass	319.90 amu	BV	119275	3063	16.60	100.00	52.59	100.00
13.770	Mass	256.90 amu	PV	36063	915	5.02	100.00	15.90	100.00

native TCDD / ^{13}C-TCDD =

272612 / 410037 = 0.6648

VERIFICATION MIXTURE 3a



Read and Understood by _____ Date _____

A2-12

native TCDD =
^{13}C-TCDD

160238 = 0.6459
248079

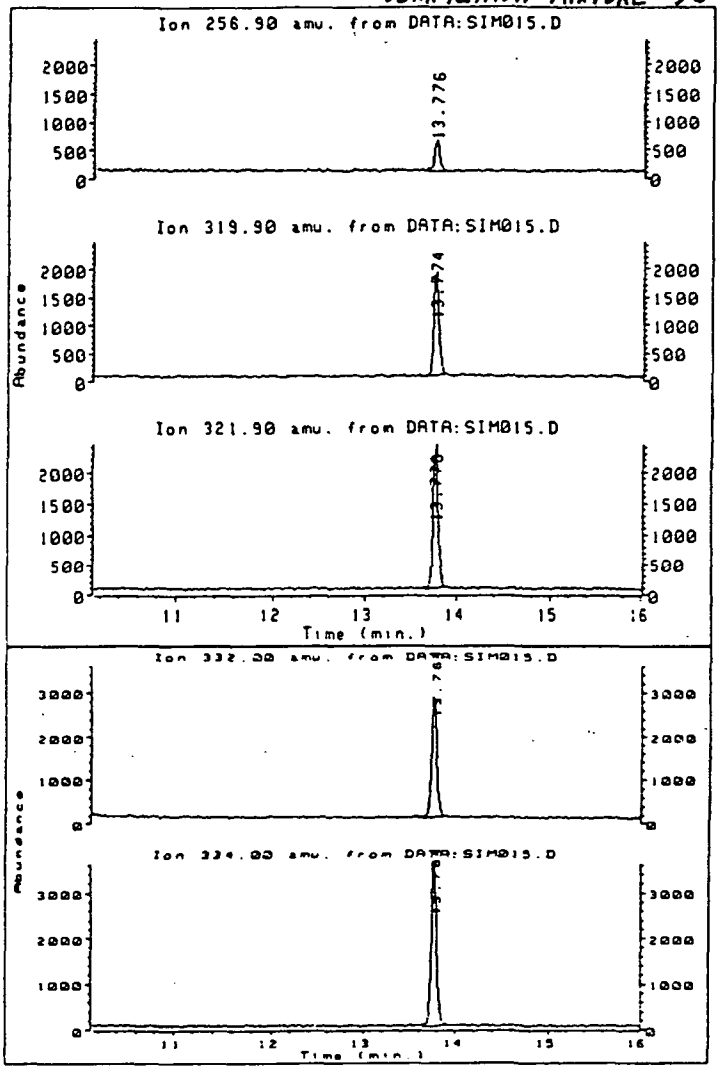
*** Area Percent ***

Report by Retention Time

Operator: B. BERRIDGE 25 Sep 90 1:17 pm
Method File Name : SIMTCDD.M
Sample Info : Verification mixture 3b 9/25/90
Misc Info: DATA:SIM015.D
Integration File Name : RESULTS.I
Bottle Number : 0

Ret Time	Signal Descr	Type	Area	Height	% Pk	% Sg	% LPk	% LSg
13.764	Mass 334.00 amu	PV	140481	3576	32.69	100.00	100.00	100.00
13.764	Mass 332.00 amu	BV	107598	2802	25.04	100.00	76.58	100.00
13.776	Mass 321.90 amu	PV	88349	2374	20.56	100.00	62.89	100.00
13.774	Mass 319.90 amu	PV	71889	1868	16.73	100.00	51.17	100.00
13.776	Mass 256.90 amu	VV	21389	574	4.98	100.00	15.23	100.00

VERIFICATION MIXTURE 3b



Read and Understood by _____ Date _____

TCDD Report Program HRTCDD.COM
2,3,7,8-TCDD by C-GC/HRMS-SIM
Revised - February 11, 1988

AER Log No.	Sample I.D.	Date Sampled	Date Extrcted	Sample Wt.(g)	Result TCDD(ppt)	320/322	332/334	Notes
)ENV007	MDC90-1	8-7-90	9-24-90	51.5	1.6	0.71	0.74	1
)ENV007	MDC90-1D	8-7-90	9-24-90	46.9	1.8	0.78	0.83	1
)ENV008	MDC90-2	8-7-90	9-24-90	52.1	2.1	0.85	0.82	
)ENV011	MDC90-6	8-7-90	9-24-90	52.2	1.9	0.81	0.80	
)ENV012	MDC90-7S	8-7-90	9-24-90	47.3	8.8	0.71	0.85	2
)ENV012	MDC90-7	8-7-90	9-24-90	50.8	2.0	0.81	0.77	
.ank	Blank		9-24-90	50.0	ND(0.58)	--	0.76	3

Duplicate sample preparation and analysis.
0.320ng native TCDD added to 47.3g MDC90-7 (equivalent to 6.8 ppt spike).
None detected. Detection limit calculated from 2.5 times noise level.

)t - parts per trillion
) - None Detected (detection limit)

File : 00003 Created : October 1, 1990 17:53
Printed : October 2, 1990 17:53

Raw Data for Sample Entries

AER og No.	13C12-TCDD Spike(ng)	Data Type	ion 257	ion 319.897	ion 321.894	ion 331.937	ion 333.934	(320+322) (332+334)
ENV007	1.912	Area		108.6	153.8	2477	3331	0.04518
ENV007	1.912	Area		166.8	212.9	3915	4705	0.04405
ENV008	1.912	Area		233.2	274.1	3963	4814	0.05780
ENV011	1.912	Area		204.4	253.7	3880	4822	0.05264
ENV012	1.912	Area		526.5	740.9	2764	3267	0.21015
ENV012	1.912	Area		262.1	325.0	4680	6068	0.05462
ank	1.912	Height		5-N	5-N	595	779	0.01820

- Noise Level
- Interfering Peak Level

Raw Data for Standard Entries

TCDD tive	(ng) 13C12	Data Type	ion 257	ion 319.897	ion 321.894	ion 331.937	ion 333.934	(320+322) (332+334)
016	1.912	Area		85.79	100.2	7202	9248	0.01131
		Height		20	16	1004	1340	0.01536
032	1.912	Area		162.5	228.5	9198	11630	0.01877
		Height		24	39	1223	1394	0.02407
064	1.912	Area		128.8	162.6	3766	4701	0.03442
		Height		19	18	543	701	0.02974
160	1.912	Area		374.5	457.9	4612	5111	0.08561
		Height		63	65	736	797	0.08350
320	1.912	Area		486.9	587.0	2770	3457	0.17246
		Height		68	98	373	479	0.19484
640	1.912	Area		733.0	989.0	2508	3125	0.30570
		Height		127	154	441	506	0.29673
601	1.912	Area		3930	5342	5316	6198	0.80528
		Height		504	749	600	693	0.96906

File : 00003

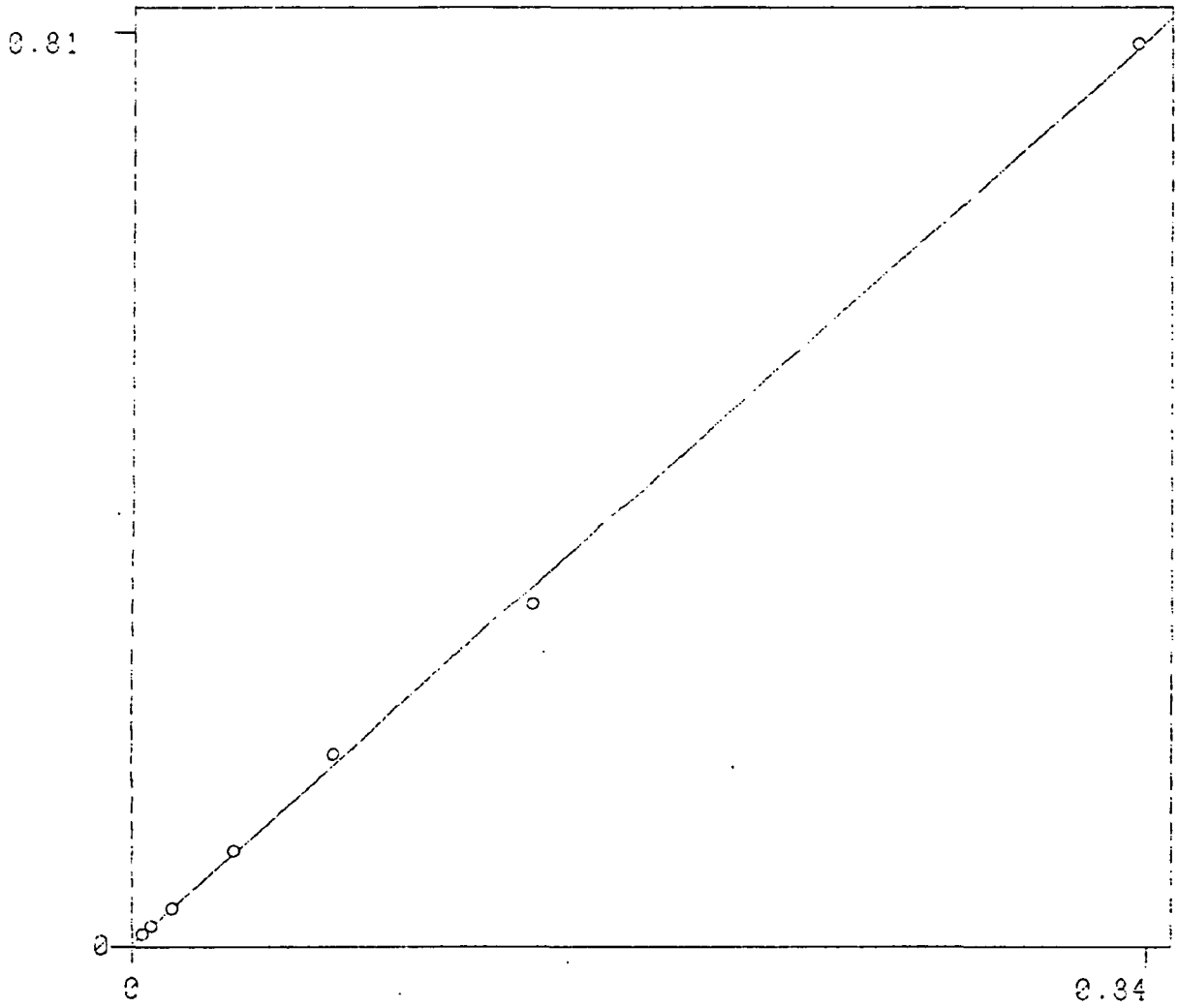
Created : October 1, 1990 17:53
Printed : October 2, 1990 17:53

X = Ratio of Amounts Native TCDD (ng) / 13C12-TCDD (ng)
Y = Ratio of SIM Areas (320 + 322) / (332 + 334)

X	Y	Y (Reg.)	% Rel. Diff (Y)
0.00837	0.01131	0.01107	2.09
0.01674	0.01877	0.01905	-1.45
0.03347	0.03442	0.03499	-1.67
0.08368	0.08561	0.08284	3.29
0.16736	0.17246	0.16257	5.90
0.33473	0.30570	0.32205	-5.21
0.83734	0.80528	0.80097	0.54

Y = 0.00310 + 0.95286 (X)

Correlation Coefficient : 0.9995978
Standard Error of Estimate : 0.0088517



Ratio of Amounts Native TCDD (ng) / 13C12-TCDD (ng)

File : 00003 Created : October 1, 1990 17:53
Printed : October 2, 1990 17:52

A3-4

Date 10/1/90

MAT 8230 C-GC-MS CONDITIONS

Column HP-5 50 m x 0.2 mm 0.33 µm film

Injector 250°C Splitless 30 PSI He

GC Oven Program 160°C (2 min) 25°C/min → 270°C (20 min)

Separator 280°C (755)

Line of Sight 290°C (770)

Ion Source EI 200°C 1mA 70eV

Ua/Ub 815

Y1 466

Y2 603

X1 522

X2 497

L1 454

L2 418

S1 0.2

Z1 549

Z2 550

P 541

Filter 330 Hz

Multiplier 2.1 KV (500)

MSCHAR 200 : 10 : 40 : 25 : 6 : 131000

HR Slits S-586 C-582 Resolution 7000

LR Slits S-594 C-804 Resolution 1000

HR : Ion 331 Resp.(V) 3.2V LR : Ion 331 Resp.(V) 30V

LR/HR Resp. ~10

A3-5

SSX: SLIST of DM00:[300,303]PFK.DAT;2
Finnigan MAT Oct 1 90 07:58:32 Page: 1

Spectrum Number: 2
Number of Peaks: 494

Norm. Factors: 1. 3287.84

PEAK#	MASS	A	B
19	69.0312	328784.	100.00
29	93.0156	5808.	1.77
34	100.0469	17408.	5.29
38	113.2344	6480.	1.97
41	119.2188	89840.	27.32
44	131.0469	84208.	25.61
50	143.0156	6432.	1.96
55	151.0469	10416.	3.17
61	162.0313	8992.	2.73
62	163.0625	3824.	1.16
66	169.0313	73600.	22.39
71	181.0156	70848.	21.55
78	193.0469	11616.	3.53
83	201.0156	3936.	1.20
84	205.0312	5712.	1.74
86	207.1094	5424.	1.65
94	219.0469	34560.	10.51
101	231.0313	40448.	12.30
108	243.0312	15280.	4.65
117	255.0469	6496.	1.98
123	267.0156	5776.	1.76
125	269.0156	20576.	6.26
131	281.0156	28464.	8.66
142	293.0000	12944.	3.94
149	305.0156	5760.	1.75
154	317.0469	4352.	1.32
156	319.0313	10784.	3.28
165	331.0156	21648.	6.58
172	342.9844	13424.	4.08
180	355.0000	5904.	1.80
188	369.0156	4208.	1.28
196	381.0156	16048.	4.88
204	393.0469	9184.	2.79
212	405.0312	5072.	1.54
220	416.9375	4128.	1.26
229	430.9844	12992.	3.95
235	443.0000	6752.	2.05
241	455.0312	5856.	1.78
255	481.0156	9008.	2.74
261	493.0312	7904.	2.40

***** SLIST processing complete. *****

SSX: EDAC CALIBRATION RESULTS
Finnigan MAT Oct 1 90 08:00:13 Page: 1

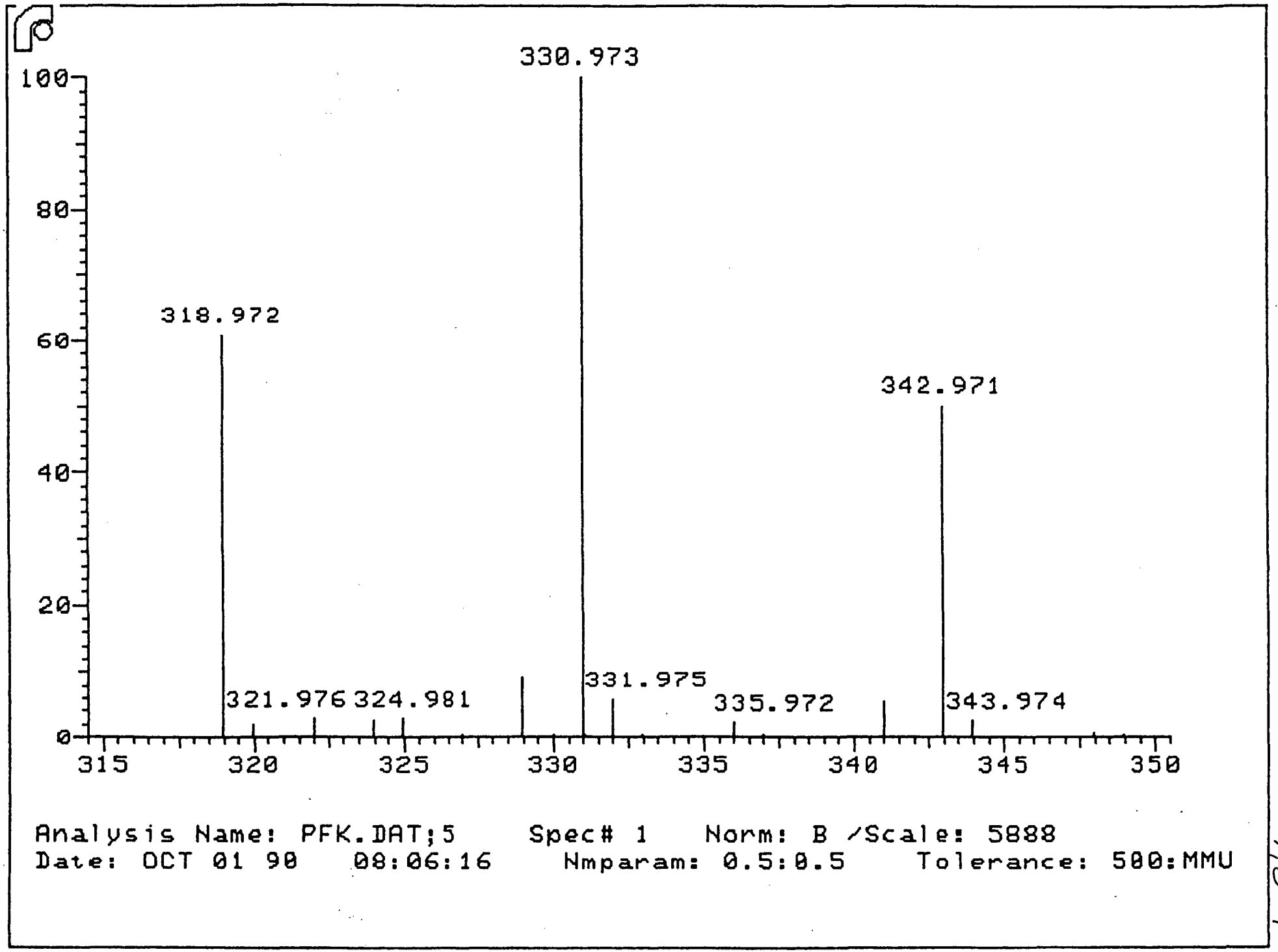
MASS CORRESPONDENCE:

SAMPLE PEAK NUMBER	SAMPLE MASS	REFERENCE MASS
1	318.9826	318.9793
23	343.2567	342.9793

EDAC CONTROL OF MASS RANGE = 1.1099

X-ACT VALUE = 661645

**** ECAL PROCESSING COMPLETE ****


330.973
100
80
318.972
60
342.971
40
20
321.976
324.981
331.975
335.972
343.974
0
315
320
325
330
335
340
345
350
Analysis Name: PFK.DAT;5
Spec# 1
Norm: B /Scale: 5888
Date: OCT 01 90
08:06:16
Nmparam: 0.5:0.5
Tolerance: 500:MMU

A3-7

SSX: MASSMENU TCDD7.MMN;2
Finnigan MAT Oct 1 90 08:11:30 Page: 4

Instrument: AP 0

Number of focussing steps was 0 jumping span was 100.0%

Menu is for a HIGH RESOLUTION ACQUISITION

Window number 1
from 17:00 to 25:00
Expected peak width is 0:12 cycle time is 1500.0 msec
Monitor 5 Channels

	Mass	Exp. Ints.	Samples	Group	
1	319.8965	1	16	1	
2	321.8937	1	16	1	
3	330.9793	16	1	1	L
4	331.9368	4	4	1	
5	333.9339	4	4	1	

(Window # 2 to 7 NOT ready for acquisition)

SSX: MASSMENU TCDD7.MMN;2
Finnigan MAT Oct 1 90 08:11:30 Page: 5

Beginning MASS MENU creation

Magnet settle time 200 msec
Magnet jump time 1000 usec
Magnet focus time 40 msec
EDAC jump time 25 msec
EDAC focus time 6 msec
EDAC capabilities: rated = 131000, calibrated = 661645
used = 661645

Window number 1

from 1774 to 2734

MASS	MDAC	EDAC	DELDAC	NSTEP	NSUM	CYCTIME
47671	47671	120644	100012	24	0	2734
47771	0	173752	0	0	20	2734
50171	0	163756	0	0	20	2734
51277	0	120644	0	0	1	2734
51374	0	115165	0	0	4	2734
51574	0	105634	0	0	4	2734

***** MASS MENU Processing complete *****

Analysis Name: DM00:[300,303]STD0.MIS;1 Window: 1

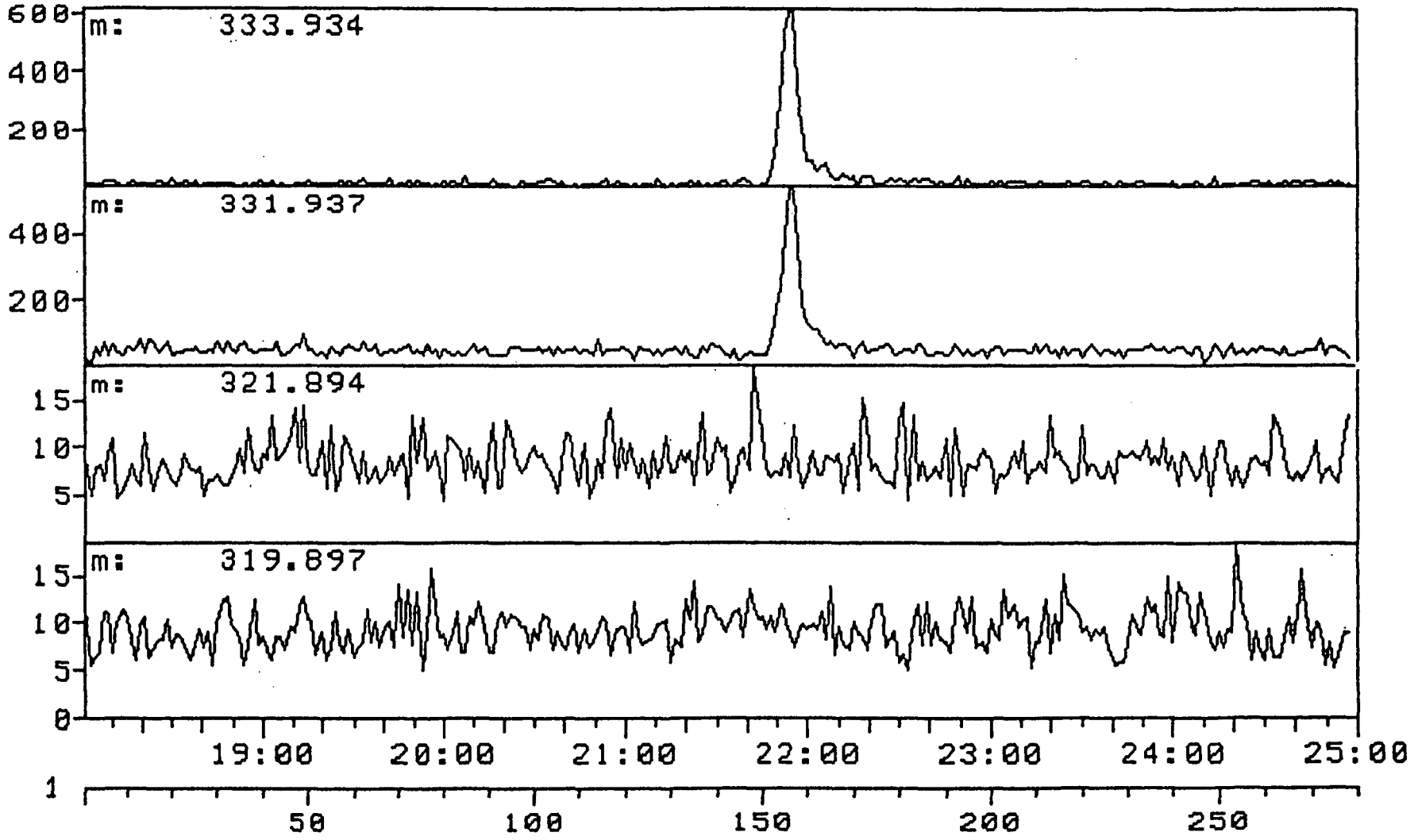
Operator: KC Spc: 5

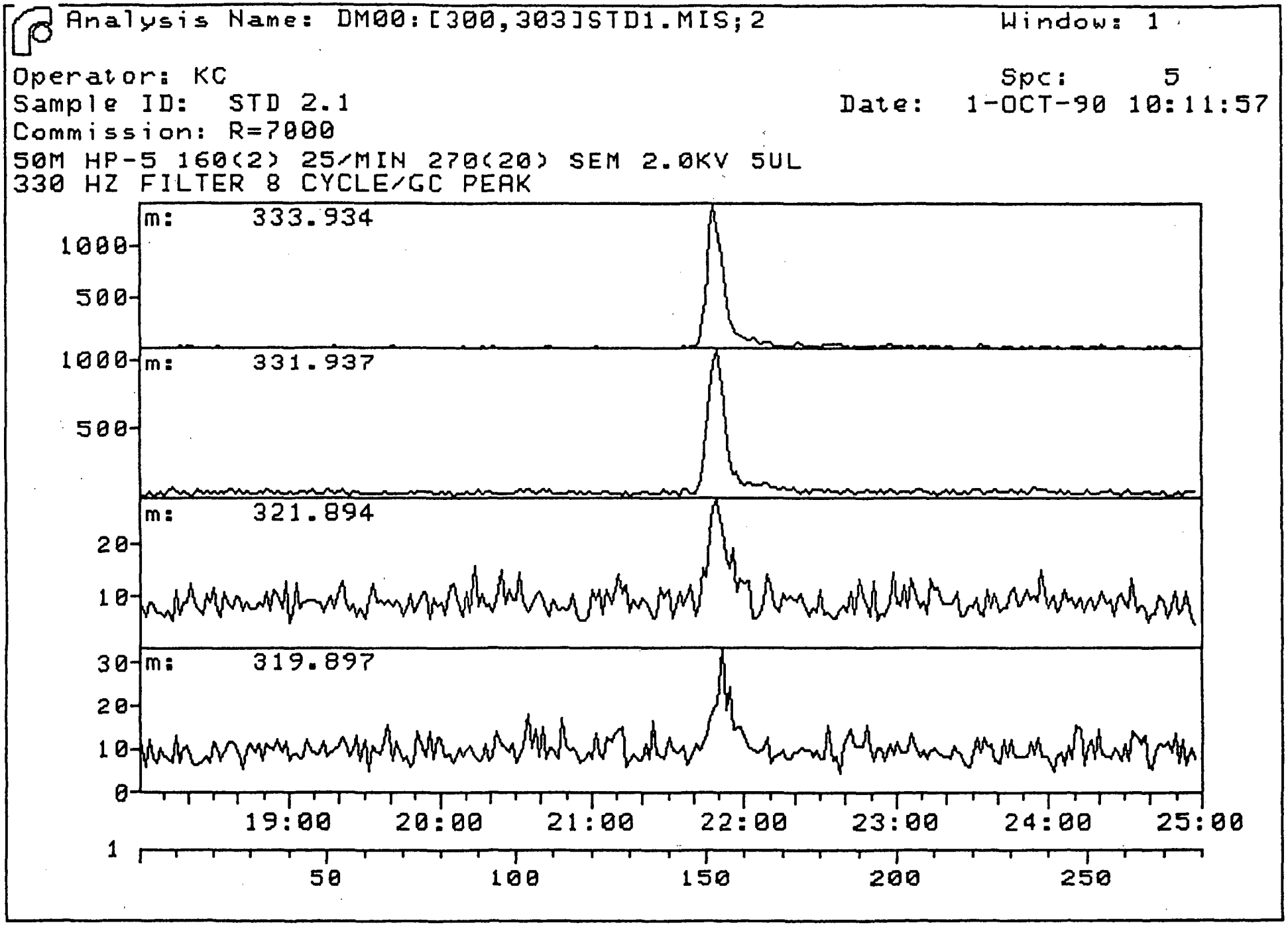
Sample ID: STD 2.0 Date: 1-OCT-90 11:12:52

Commission: R=7000

50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL

330 HZ FILTER 8 CYCLE/GC PEAK




Analysis Name: DM00:[300,303]STD1.MIS;2
Window: 1
Operator: KC
Spc: 5
Sample ID: STD 2.1
Date: 1-OCT-90 10:11:57
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.0KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
m: 331.937
m: 321.894
m: 319.897
19:00
20:00
21:00
22:00
23:00
24:00
25:00
50
100
150
200
250

A3-12

SSX: PLIST of DM00:[300,303]STD1.PEA;5
Finnigan MAT Oct 2 90 12:52:10 Page: 1

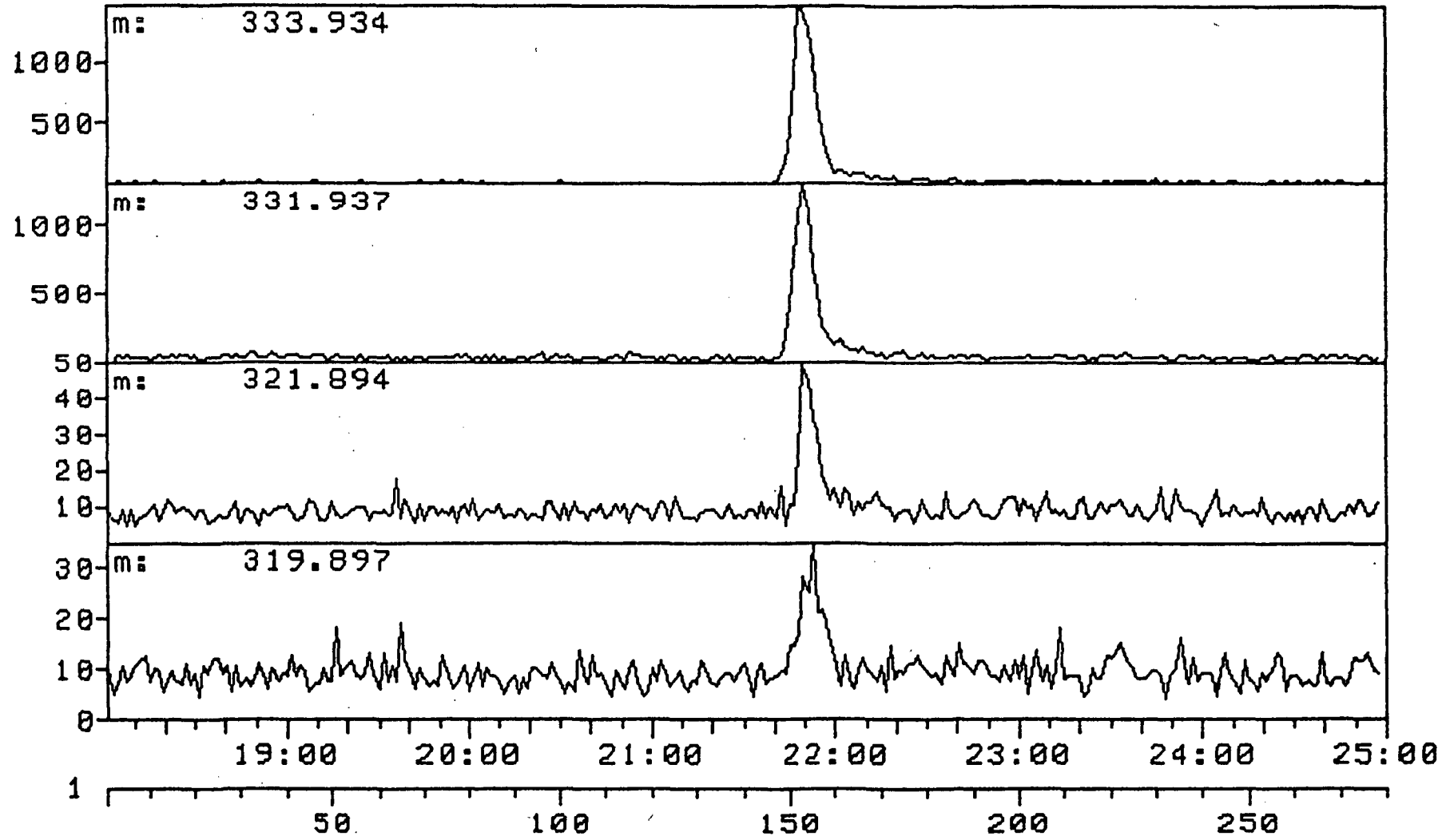
Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD 2.1
Filename: DM00:[300,303]STD1.MIS;2
Creation Date & Time: 1-OCT-90 10:11:57
Integrated Area: 1.664E+04 Integrated Height: 2380
Maximum Area: 9.248E+03 Maximum Height: 1340
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.0KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
21:51	8.579E+01	0.93	0.52	20	1.49	0.84
Trace: 321.8937						
21:49	1.002E+02	1.08	0.60	16	1.19	0.67
Trace: 331.9368						
21:49	7.202E+03	77.87	43.29	1004	74.93	42.18
Trace: 333.9339						
21:49	9.248E+03	100.00	55.59	1340	100.00	56.30

**** PLIST Processing complete ****

Analysis Name: DM00:[300,303]STD2.MIS;1 Window: 1

Operator: KC Spc: 5
Sample ID: STD 2.2 Date: 1-OCT-90 10:40:44
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
1 KHZ FILTER 8 CYCLE/GC PEAK



A3-14

SSX: PLIST of DM00:[300,303]STD2.PEA;3
Finnigan MAT Oct 2 90 11:42:33 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD 2.2
Filename: DM00:[300,303]STD2.MIS;1
Creation Date & Time: 1-OCT-90 10:40:44
Integrated Area: 2.122E+04 Integrated Height: 2680
Maximum Area: 1.163E+04 Maximum Height: 1394
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace:	319.8965					
21:52	1.625E+02	1.40	0.77	24	1.72	0.90
Trace:	321.8937					
21:52	2.285E+02	1.96	1.08	39	2.80	1.46
Trace:	331.9368					
21:50	9.198E+03	79.09	43.35	1223	87.73	45.63
Trace:	333.9339					
21:50	1.163E+04	100.00	54.81	1394	100.00	52.01

**** PLIST Processing complete ****

Analysis Name: DM00:[300,303]STD3.MIS;1 Window: 1

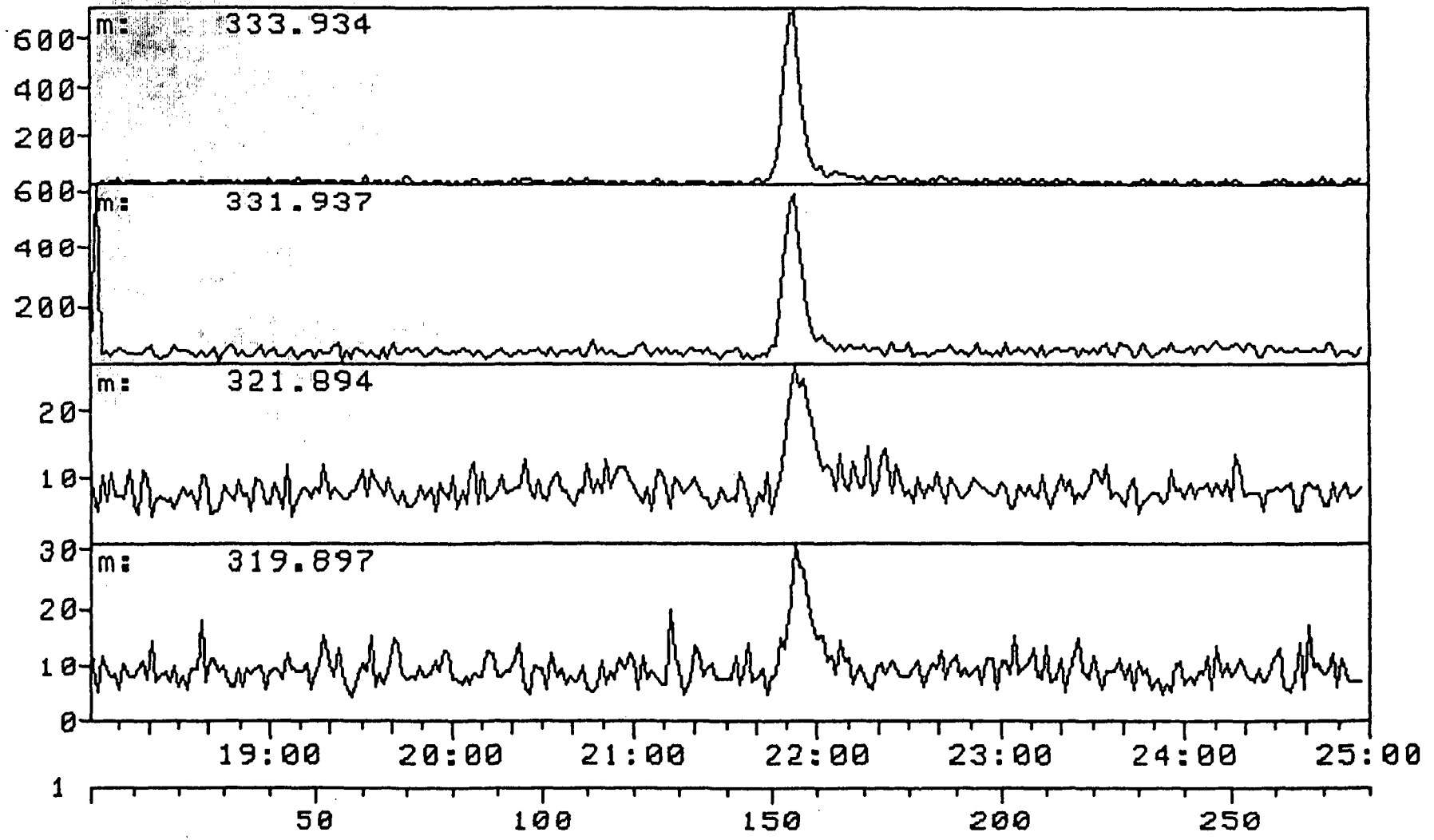
Operator: KC Spc: 5

Sample ID: STD 2.3 Date: 1-OCT-90 11:41:13

Commission: R=7000

50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL

330 HZ FILTER 8 CYCLE/GC PEAK



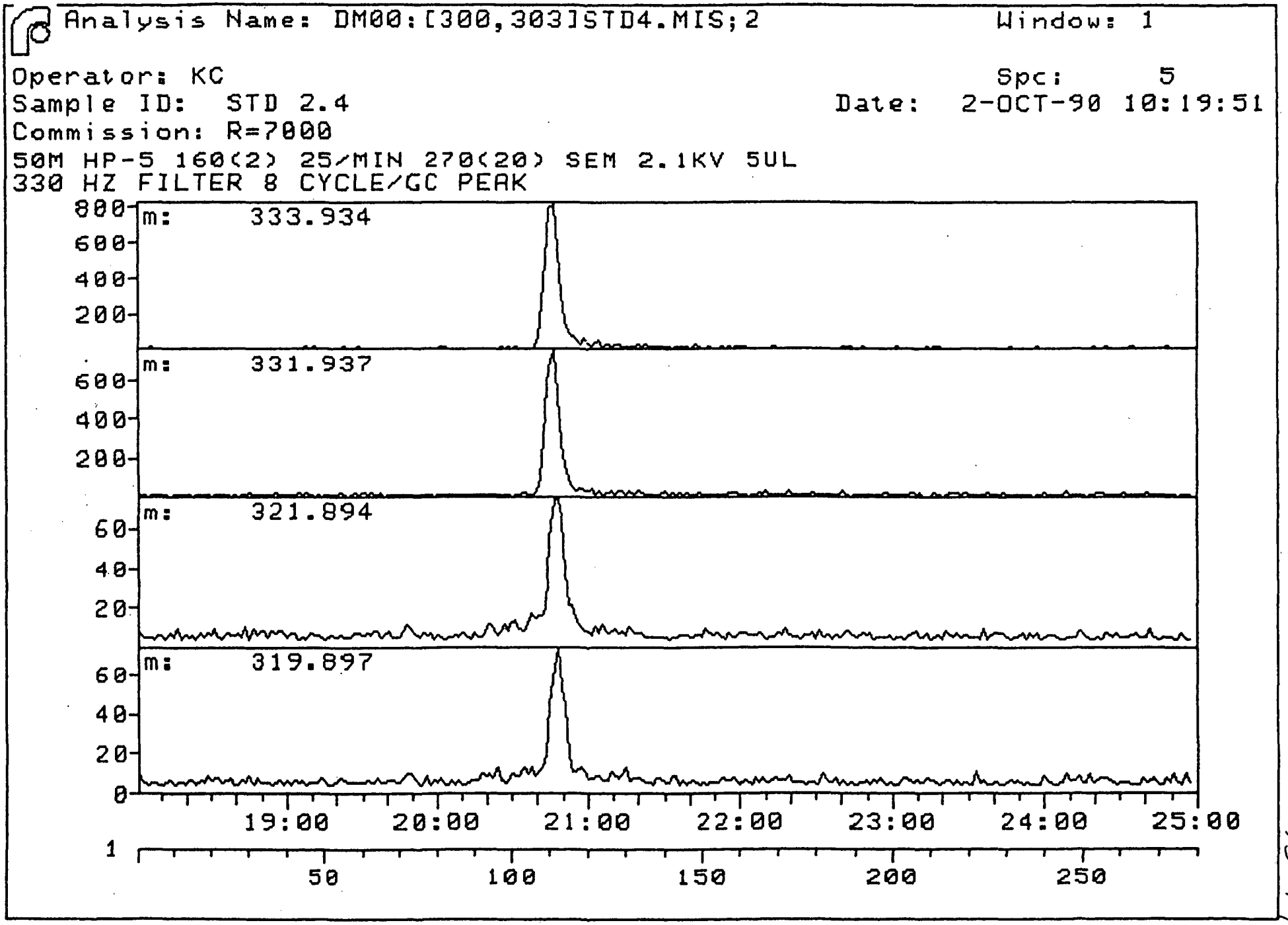
A3-16

SSX: PLIST of DM00:[300,303]STD3.PEA;1
Finnigan MAT Oct 1 90 14:32:19 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD 2.3
Filename: DM00:[300,303]STD3.MIS;1
Creation Date & Time: 1-OCT-90 11:41:13
Integrated Area: 8.758E+03 Integrated Height: 1281
Maximum Area: 4.701E+03 Maximum Height: 701
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace:	319.8965					
21:55	1.288E+02	2.74	1.47	19	2.71	1.48
Trace:	321.8937					
21:56	1.626E+02	3.46	1.86	18	2.57	1.41
Trace:	331.9368					
21:53	3.766E+03	80.11	43.00	543	77.46	42.39
Trace:	333.9339					
21:52	4.701E+03	100.00	53.68	701	100.00	54.72

**** PLIST Processing complete ****


Analysis Name: DM00:[300,303]STD4.MIS;2
Window: 1
Operator: KC
Spc: 5
Sample ID: STD 2.4
Date: 2-OCT-90 10:19:51
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
m: 331.937
m: 321.894
m: 319.897
800
600
400
200
600
400
200
60
40
20
60
40
20
0
19:00
20:00
21:00
22:00
23:00
24:00
25:00
1
50
100
150
200
250

A3-17

SSX: PLIST of DM00:[300,303]STD4.PEA;2
Finnigan MAT Oct 2 90 11:06:59 Page: 1

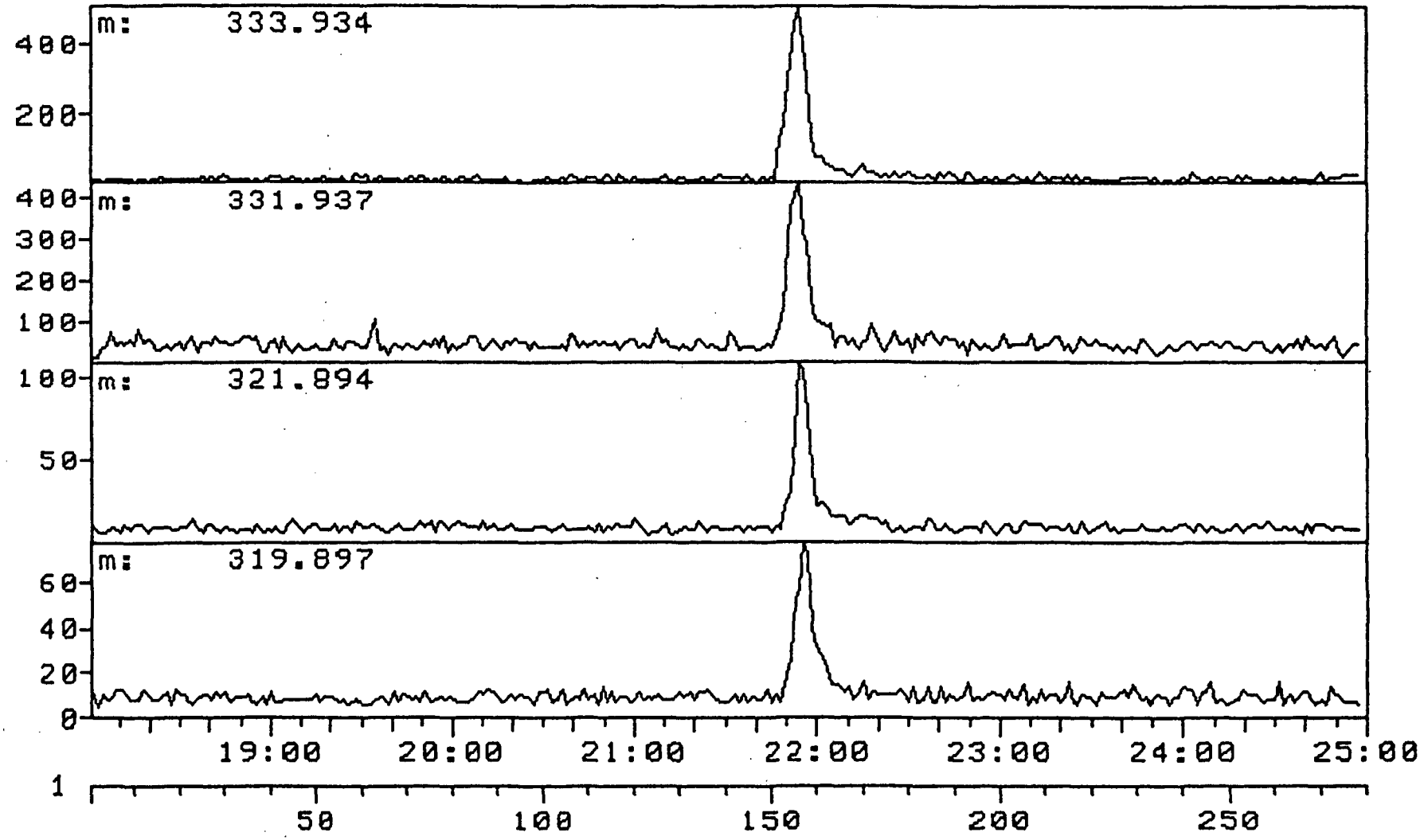
Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD 2.4
Filename: DM00:[300,303]STD4.MIS;2
Creation Date & Time: 2-OCT-90 10:19:51
Integrated Area: 1.056E+04 Integrated Height: 1661
Maximum Area: 5.111E+03 Maximum Height: 797
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
20:48	3.745E+02	7.33	3.55	63	7.90	3.79
Trace: 321.8937						
20:47	4.579E+02	8.96	4.34	65	8.16	3.91
Trace: 331.9368						
20:46	4.612E+03	90.25	43.70	736	92.35	44.31
Trace: 333.9339						
20:46	5.111E+03	100.00	48.42	797	100.00	47.98

**** PLIST Processing complete ****

Analysis Name: DM00:[300,303]STD5.MIS;1 Window: 1

Operator: KC Spc: 5
Sample ID: STD 2.5 Date: 1-OCT-90 12:41:57
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK



A3-20

SSX: PLIST of DM00:[300,303]STD5.PEA;1
Finnigan MAT Oct 2 90 09:56:42 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD 2.5
Filename: DM00:[300,303]STD5.MIS;1
Creation Date & Time: 1-OCT-90 12:41:57
Integrated Area: 7.301E+03 Integrated Height: 1018
Maximum Area: 3.457E+03 Maximum Height: 479
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
21:56	4.869E+02	14.08	6.67	68	14.20	6.68
Trace: 321.8937						
21:55	5.870E+02	16.98	8.04	98	20.46	9.63
Trace: 331.9368						
21:54	2.770E+03	80.11	37.94	373	77.87	36.64
Trace: 333.9339						
21:54	3.457E+03	100.00	47.35	479	100.00	47.05

**** PLIST Processing complete ****

0.37 / 1.9

Analysis Name: DM00:[300,303]STD6.MIS;1 Window: 1

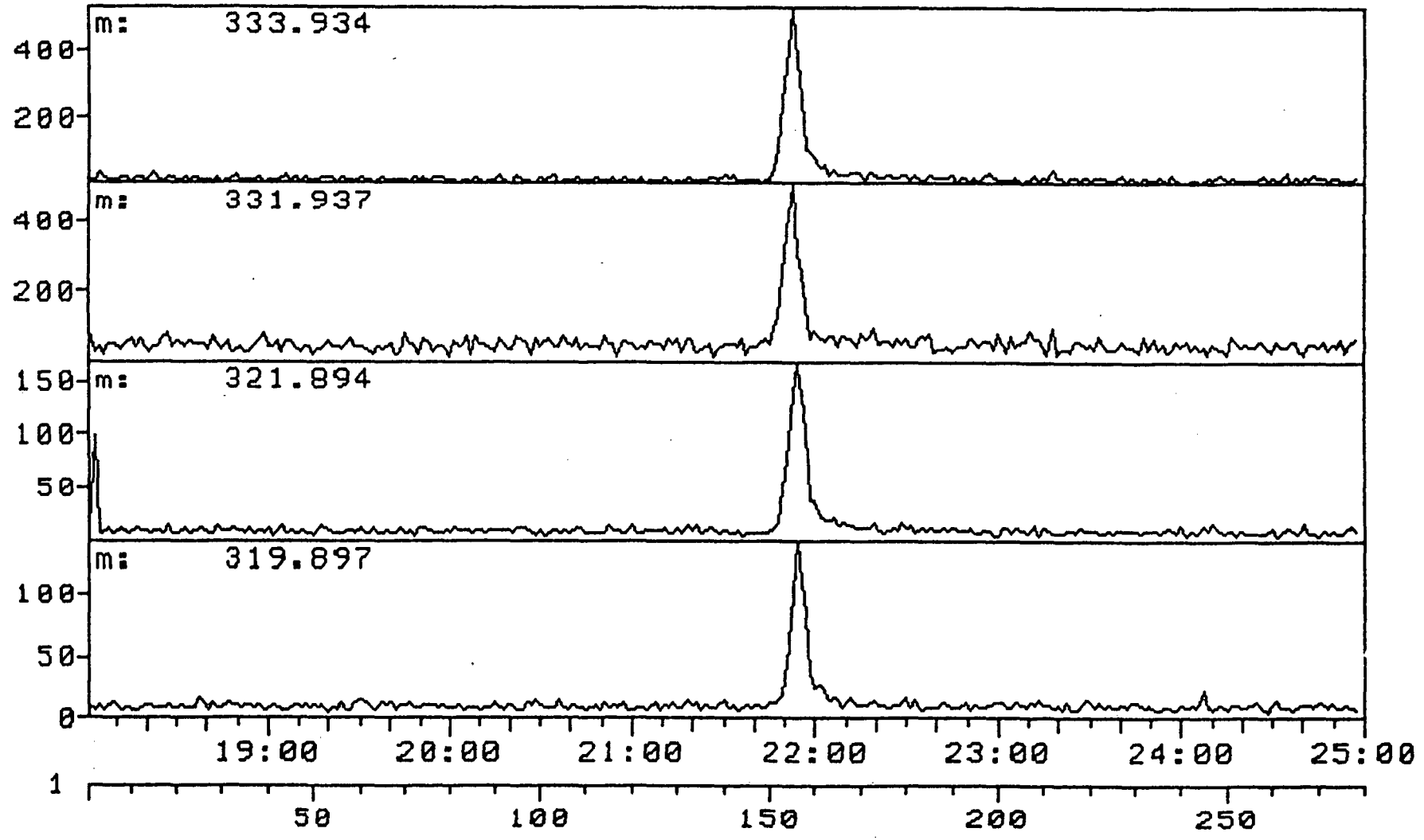
Operator: KC Spc: 5

Sample ID: STD 2.6 Date: 1-OCT-90 13:09:56

Commission: R=7000

50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL

330 HZ FILTER 8 CYCLE/GC PEAK



A3-21

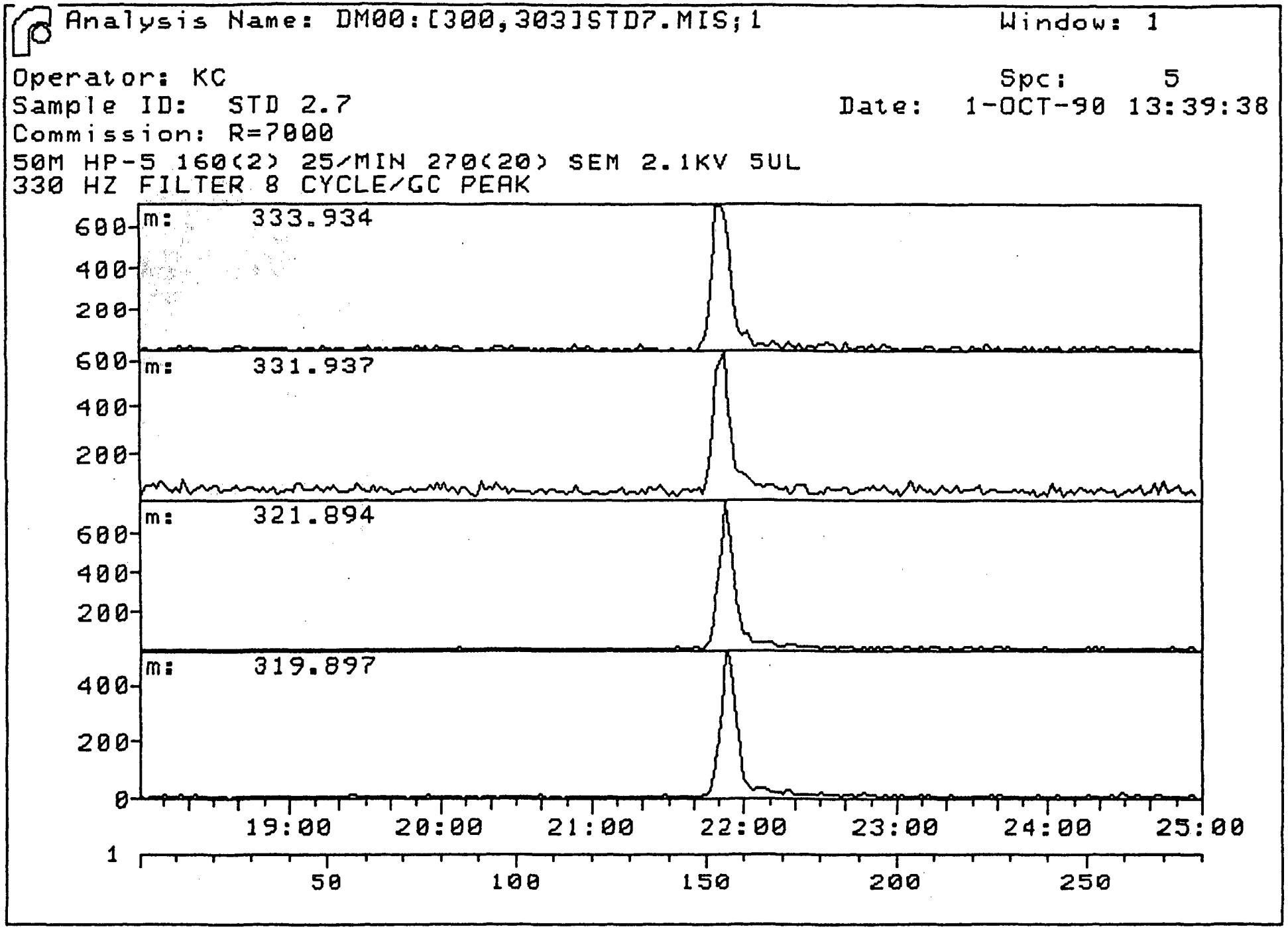
SSX: PLIST of DM00:[300,303]STD6.PEA;1
Finnigan MAT Oct 2 90 09:59:56 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD 2.6
Filename: DM00:[300,303]STD6.MIS;1
Creation Date & Time: 1-OCT-90 13:09:56
Integrated Area: 7.355E+03 Integrated Height: 1228
Maximum Area: 3.125E+03 Maximum Height: 506
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
21:55	7.330E+02	23.45	9.97	127	25.10	10.34
Trace: 321.8937						
21:54	9.890E+02	31.65	13.45	154	30.43	12.54
Trace: 331.9368						
21:53	2.508E+03	80.25	34.10	441	87.15	35.91
Trace: 333.9339						
21:53	3.125E+03	100.00	42.49	506	100.00	41.21

**** PLIST Processing complete ****

0.64 / 1.92


Analysis Name: DM00:[300,303]STD7.MIS;1
Window: 1
Operator: KC
Spc: 5
Sample ID: STD 2.7
Date: 1-OCT-90 13:39:38
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
m: 331.937
m: 321.894
m: 319.897
600
400
200
0
19:00
20:00
21:00
22:00
23:00
24:00
25:00
1
50
100
150
200
250

A3-24

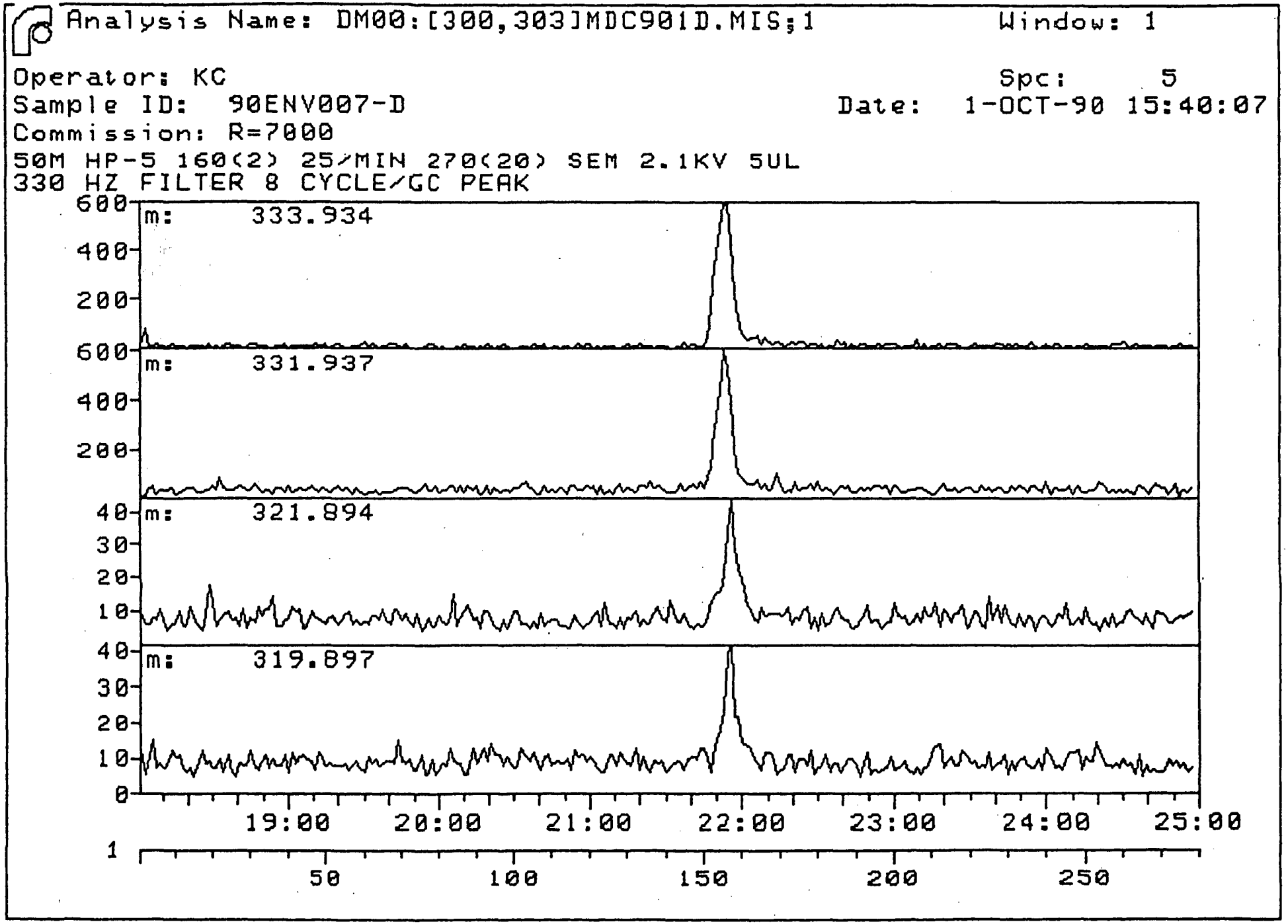
SSX: PLIST of DM00:[300,303]STD7.PEA;1
Finnigan MAT Oct 1 90 14:49:53 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD 2.7
Filename: DM00:[300,303]STD7.MIS;1
Creation Date & Time: 1-OCT-90 13:39:38
Integrated Area: 2.079E+04 Integrated Height: 2546
Maximum Area: 6.198E+03 Maximum Height: 749
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
21:55	3.930E+03	63.40	18.91	504	67.29	19.80
Trace: 321.8937						
21:54	5.342E+03	86.19	25.70	749	100.00	29.42
Trace: 331.9368						
21:54	5.316E+03	85.77	25.58	600	80.11	23.57
Trace: 333.9339						
21:53	6.198E+03	100.00	29.82	693	92.52	27.22

**** PLIST Processing complete ****

1.6-1 / 1-91

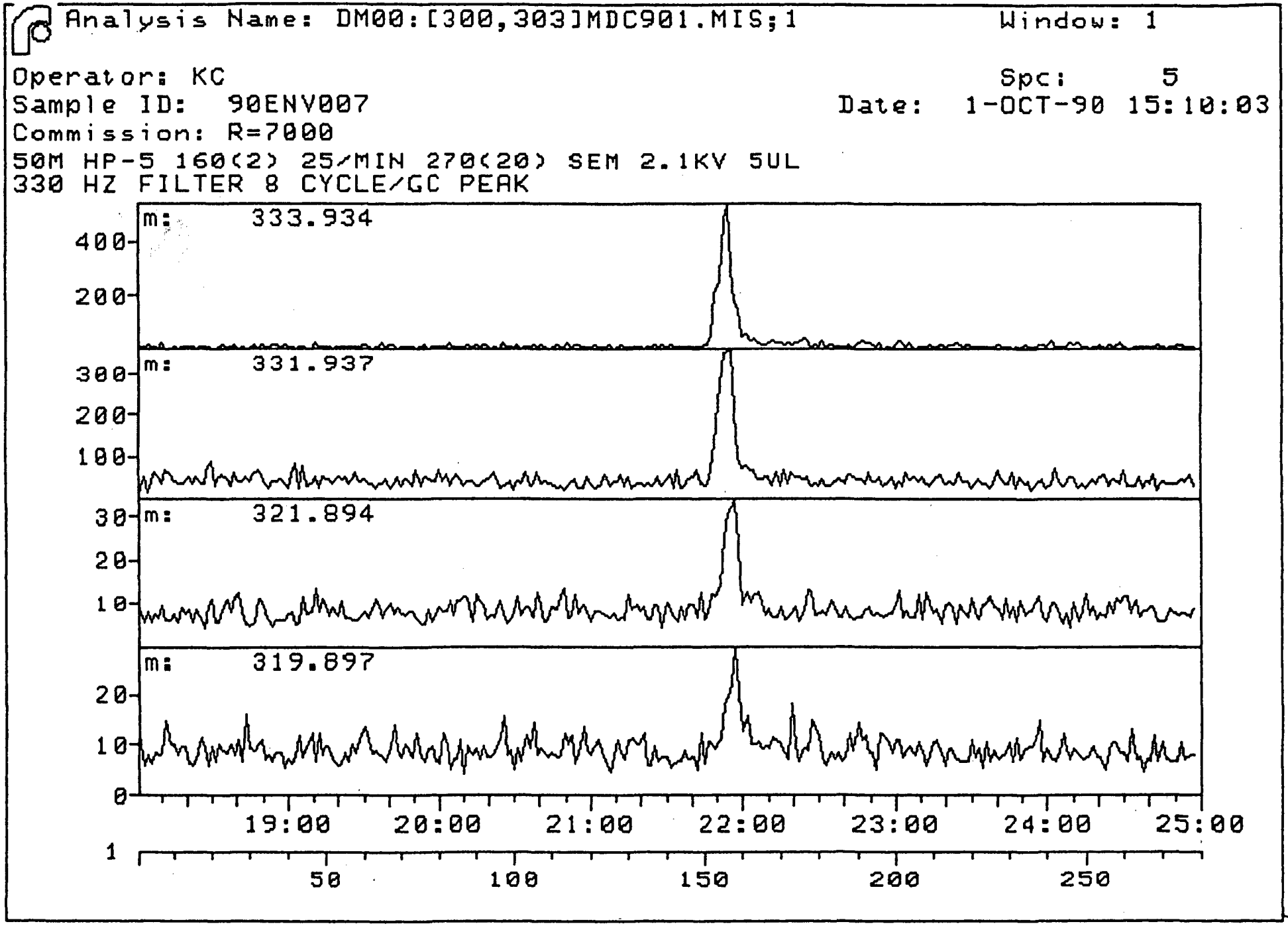

Analysis Name: DM00:[300,303]MDC901D.MIS;1
Window: 1
Operator: KC
Spc: 5
Sample ID: 90ENV007-D
Date: 1-OCT-90 15:40:07
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
m: 331.937
m: 321.894
m: 319.897
600
400
200
600
400
200
40
30
20
10
40
30
20
10
0
19:00
20:00
21:00
22:00
23:00
24:00
25:00
1
50
100
150
200
250

SSX: PLIST of DM00:[300,303]MDC901D.PEA;2
Finnigan MAT Oct 2 90 13:17:43 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: 90ENV007-D
Filename: DM00:[300,303]MDC901D.MIS;1
Creation Date & Time: 1-OCT-90 15:40:07
Integrated Area: 9.000E+03 Integrated Height: 1212
Maximum Area: 4.705E+03 Maximum Height: 583
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
21:55	1.668E+02	3.54	1.85	31	5.32	2.56
Trace: 321.8937						
21:55	2.129E+02	4.53	2.37	35	6.00	2.89
Trace: 331.9368						
21:54	3.915E+03	83.21	43.50	563	96.57	46.45
Trace: 333.9339						
21:54	4.705E+03	100.00	52.28	583	100.00	48.10

**** PLIST Processing complete ****


Analysis Name: DM00:[300,303]MDC901.MIS;1
Window: 1
Operator: KC
Spc: 5
Sample ID: 90ENV007
Date: 1-OCT-90 15:10:03
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
m: 331.937
m: 321.894
m: 319.897
19:00
20:00
21:00
22:00
23:00
24:00
25:00
50
100
150
200
250

A3-28

SSX: PLIST of DM00:[300,303]MDC901.PEA;1
Finnigan MAT Oct 1 90 15:53:27 Page: 1

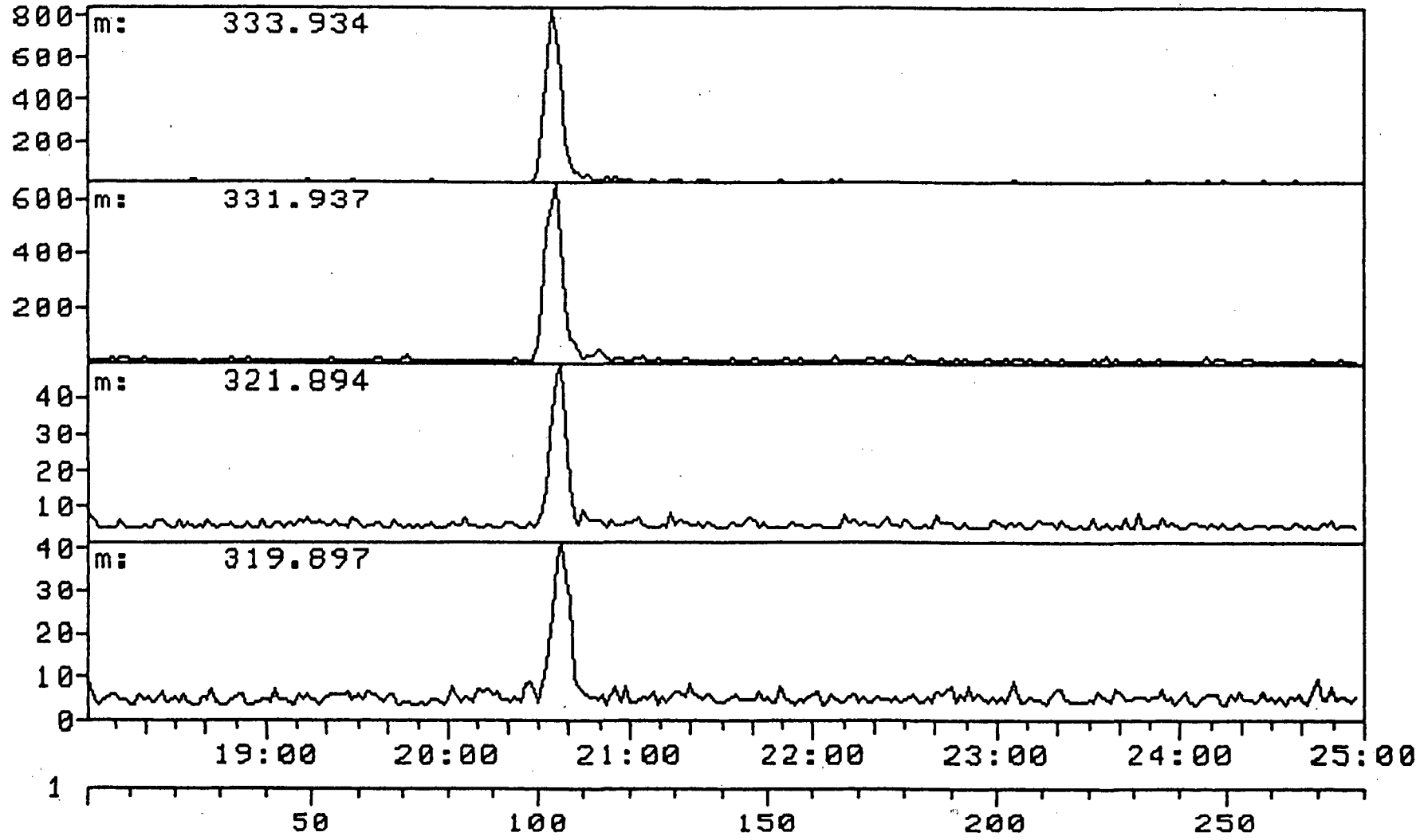
Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: 90ENV007
Filename: DM00:[300,303]MDC901.MIS;1
Creation Date & Time: 1-OCT-90 15:10:03
Integrated Area: 6.070E+03 Integrated Height: 879
Maximum Area: 3.331E+03 Maximum Height: 518
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
21:57	1.086E+02	3.26	1.79	19	3.67	2.16
Trace: 321.8937						
21:55	1.538E+02	4.62	2.53	24	4.63	2.73
Trace: 331.9368						
21:54	2.477E+03	74.36	40.80	318	61.39	36.18
Trace: 333.9339						
21:54	3.331E+03	100.00	54.87	518	100.00	58.93

**** PLIST Processing complete ****

Analysis Name: DM00:[300,303]MDC902.MIS;2 Window: 1

Operator: KC Spc: 5
Sample ID: 90ENV008 Date: 1-OCT-90 18:39:23
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK

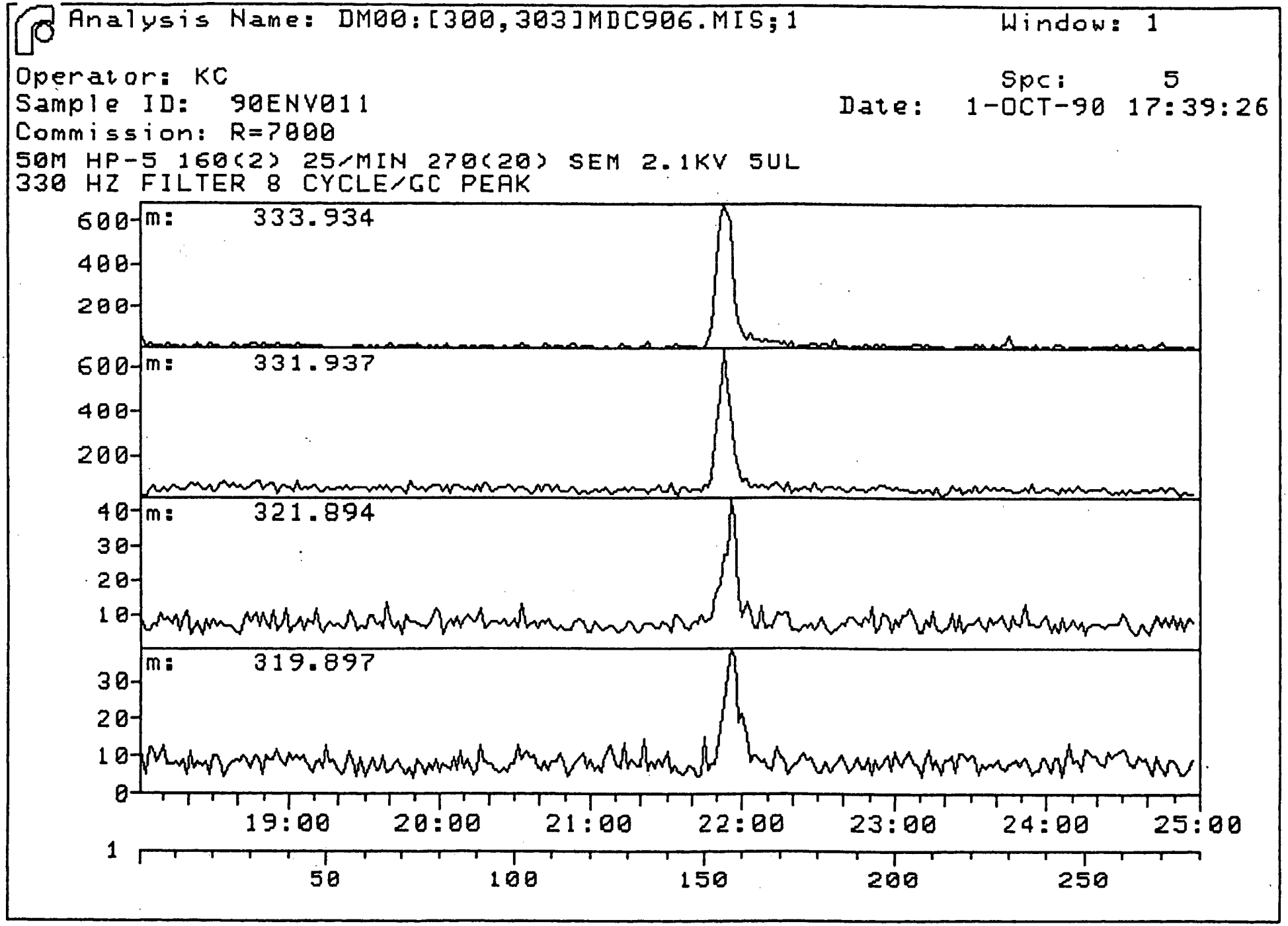


SSX: PLIST of DM00:[300,303]MDC902.PEA;1
Finnigan MAT Oct 2 90 11:54:08 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: 90ENV008
Filename: DM00:[300,303]MDC902.MIS;2
Creation Date & Time: 1-OCT-90 18:39:23
Integrated Area: 9.284E+03 Integrated Height: 1539
Maximum Area: 4.814E+03 Maximum Height: 824
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
20:37	2.332E+02	4.84	2.51	36	4.37	2.34
Trace: 321.8937						
20:37	2.741E+02	5.69	2.95	44	5.34	2.86
Trace: 331.9368						
20:35	3.963E+03	82.31	42.68	635	77.06	41.26
Trace: 333.9339						
20:35	4.814E+03	100.00	51.85	824	100.00	53.54

**** PLIST Processing complete ****


Analysis Name: DM00:[300,303]MDC906.MIS;1
Window: 1
Operator: KC
Spc: 5
Sample ID: 90ENV011
Date: 1-OCT-90 17:39:26
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
m: 331.937
m: 321.894
m: 319.897
600
400
200
40
30
20
10
0
19:00
20:00
21:00
22:00
23:00
24:00
25:00
1
50
100
150
200
250

A3-32

SSX: PLIST of DM00:[300,303]MDC906.PEA;1
Finnigan MAT Oct 2 90 12:04:39 Page: 1

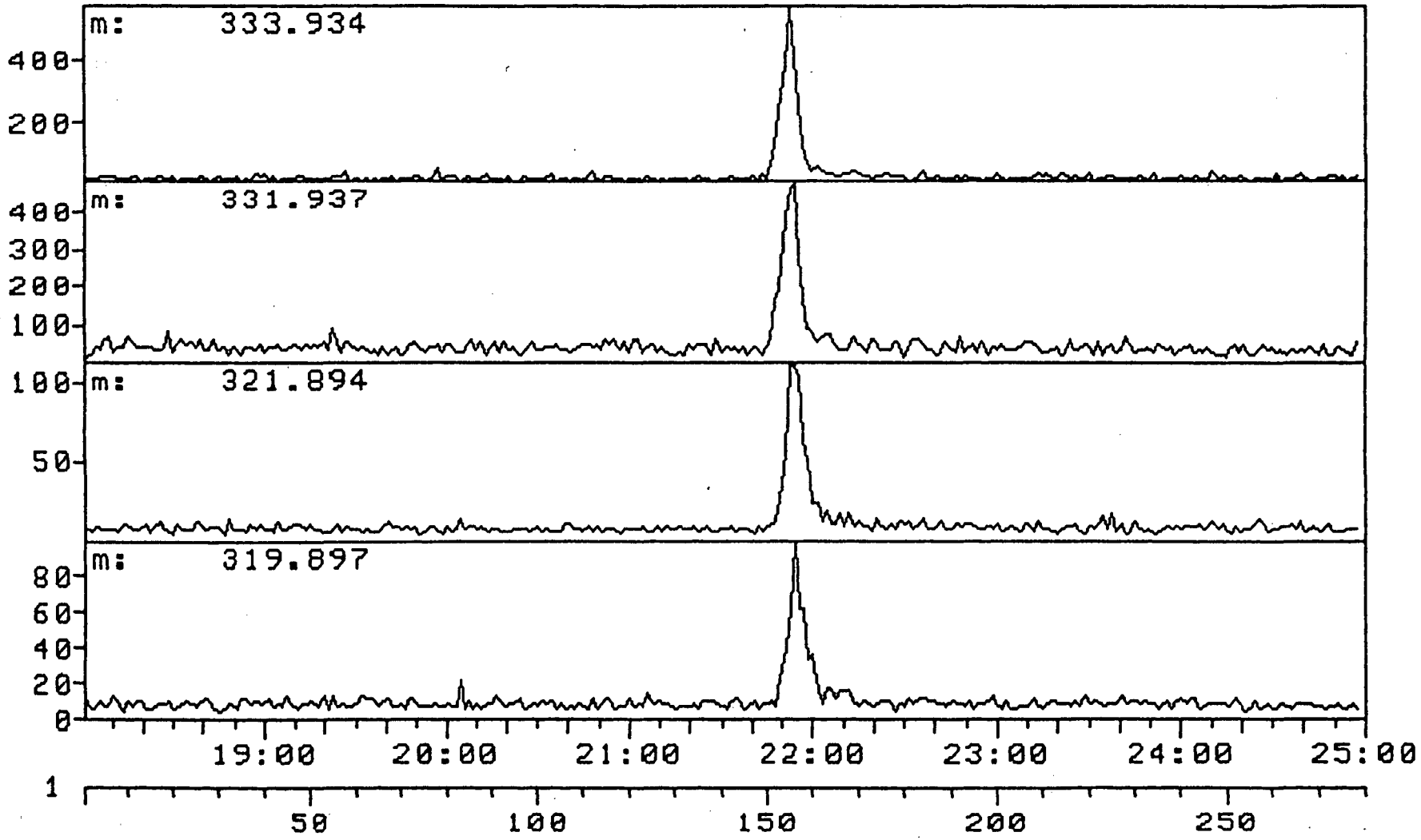
Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: 90ENV011
Filename: DM00:[300,303]MDC906.MIS;1
Creation Date & Time: 1-OCT-90 17:39:26
Integrated Area: 9.160E+03 Integrated Height: 1354
Maximum Area: 4.822E+03 Maximum Height: 654
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace:	319.8965					
21:56	2.044E+02	4.24	2.23	30	4.59	2.22
Trace:	321.8937					
21:55	2.537E+02	5.26	2.77	37	5.66	2.73
Trace:	331.9368					
21:53	3.880E+03	80.47	42.36	633	96.79	46.75
Trace:	333.9339					
21:53	4.822E+03	100.00	52.64	654	100.00	48.30

**** PLIST Processing complete ****

Analysis Name: DM00:[300,303]MDC907S.MIS;1 Window: 1

Operator: KC Spc: 5
Sample ID: STD ADDN Date: 1-OCT-90 16:40:56
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK



SSX: PLIST of DM00:[300,303]MDC907S.PEA;1
Finnigan MAT Oct 2 90 12:10:27 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: STD ADDN
Filename: DM00:[300,303]MDC907S.MIS;1
Creation Date & Time: 1-OCT-90 16:40:56
Integrated Area: 7.298E+03 Integrated Height: 1171
Maximum Area: 3.267E+03 Maximum Height: 555
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace: 319.8965						
21:55	5.265E+02	16.12	7.21	90	16.22	7.69
Trace: 321.8937						
21:55	7.409E+02	22.68	10.15	102	18.38	8.71
Trace: 331.9368						
21:53	2.764E+03	84.61	37.87	424	76.40	36.21
Trace: 333.9339						
21:53	3.267E+03	100.00	44.76	555	100.00	47.40

**** PLIST Processing complete ****

Analysis Name: DM00:[300,303]MDC907.MIS;2 Window: 1

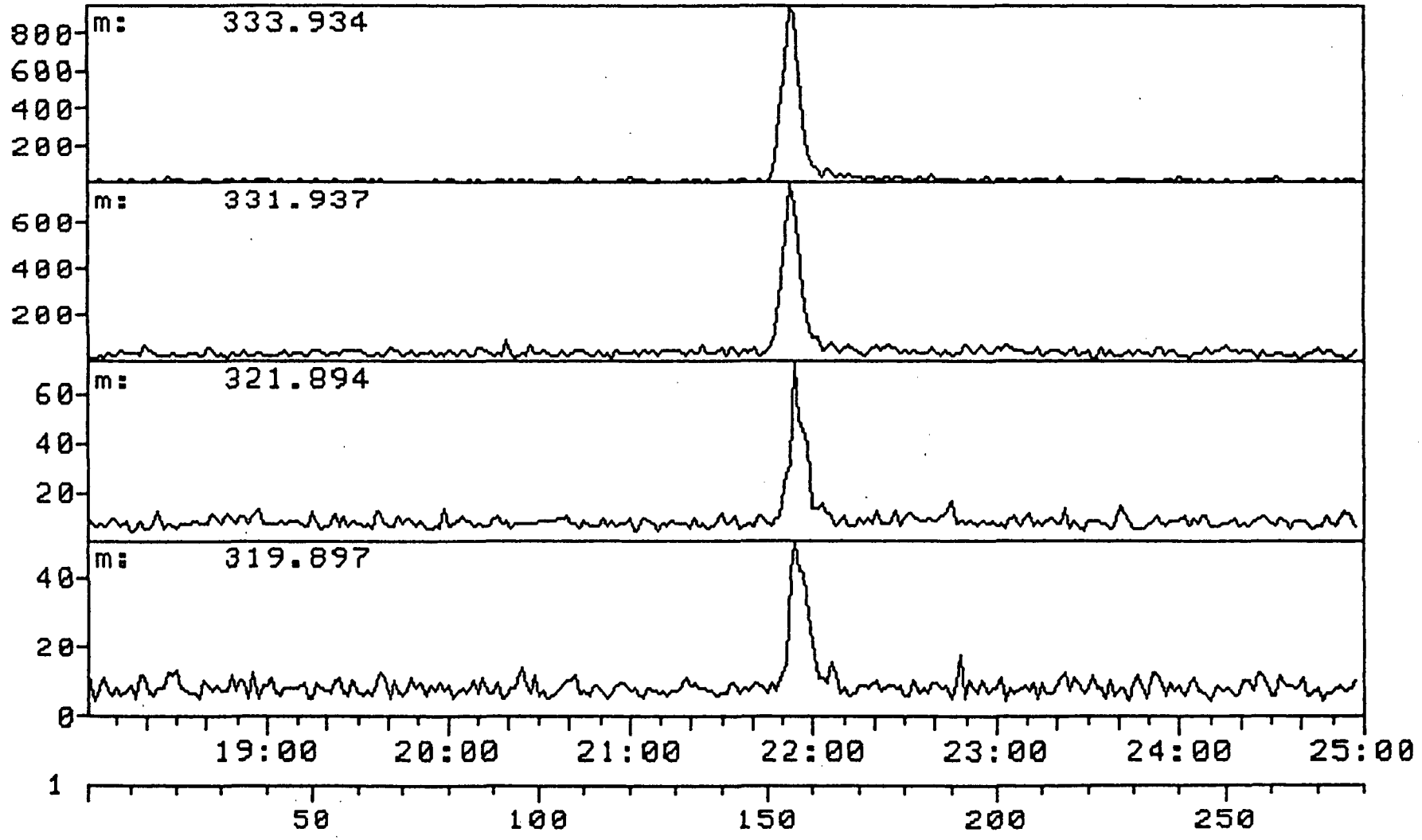
Operator: KC Spc: 5

Sample ID: 90ENV012 Date: 1-OCT-90 17:09:25

Commission: R=7000

50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL

330 HZ FILTER 8 CYCLE/GC PEAK



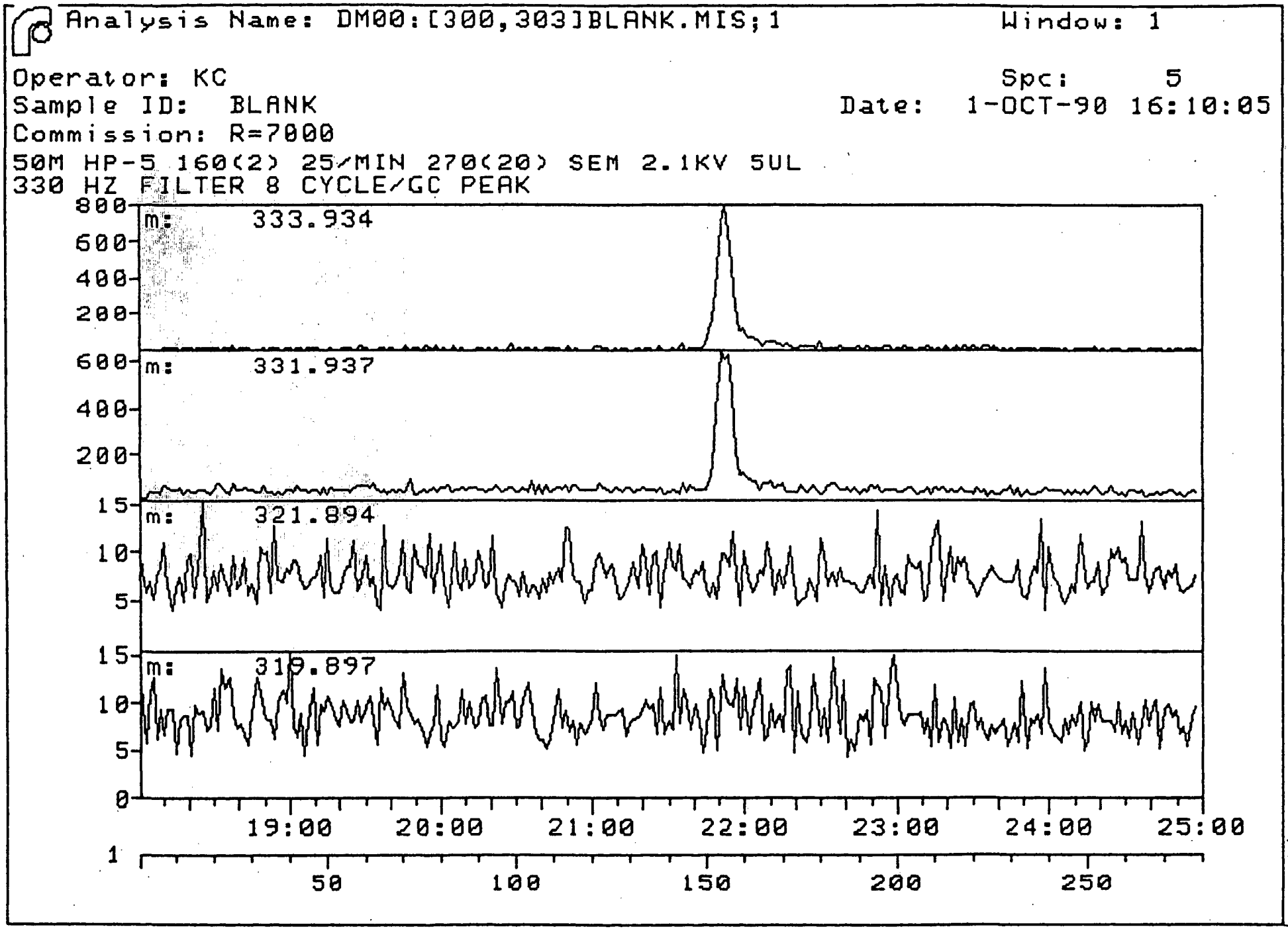
A3-36

SSX: PLIST of DM00:[300,303]MDC907.PEA;1
Finnigan MAT Oct 2 90 12:06:49 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: 90ENV012
Filename: DM00:[300,303]MDC907.MIS;2
Creation Date & Time: 1-OCT-90 17:09:25
Integrated Area: 1.134E+04 Integrated Height: 1753
Maximum Area: 6.068E+03 Maximum Height: 926
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace:	319.8965					
21:55	2.621E+02	4.32	2.31	41	4.43	2.34
Trace:	321.8937					
21:55	3.250E+02	5.36	2.87	63	6.80	3.59
Trace:	331.9368					
21:53	4.680E+03	77.13	41.29	723	78.08	41.24
Trace:	333.9339					
21:53	6.068E+03	100.00	53.53	926	100.00	52.82

**** PLIST Processing complete ****


Analysis Name: DM00:[300,303]BLANK.MIS;1
Window: 1
Operator: KC
Spc: 5
Sample ID: BLANK
Date: 1-OCT-90 16:10:05
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 5UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
m: 331.937
m: 321.894
m: 319.897
800
600
400
200
600
400
200
15
10
5
15
10
5
0
19:00
20:00
21:00
22:00
23:00
24:00
25:00
1
50
100
150
200
250

A3-38

SSX: PLIST of DM00:[300,303]BLANK.PEA;1
Finnigan MAT Oct 2 90 17:18:44 Page: 1

Calibration curve not well-defined for
Area , Height - use PPLOT to examine data
Sample Identification: BLANK
Filename: DM00:[300,303]BLANK.MIS;1
Creation Date & Time: 1-OCT-90 16:10:05
Integrated Area: 1.099E+04 Integrated Height: 1384
Maximum Area: 5.903E+03 Maximum Height: 779
Comment: 50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV
5UL

Time	AREA			HEIGHT		
Centroid	Abs	Base	Sum	Abs	Base	Sum
Trace:	319.8965					
21:59	3.166E+01	0.54	0.29	5	0.64	0.36
Trace:	321.8937					
21:58	3.220E+01	0.55	0.29	5	0.64	0.36
Trace:	331.9368					
21:54	5.026E+03	85.14	45.72	595	76.38	42.99
Trace:	333.9339					
21:54	5.903E+03	100.00	53.70	779	100.00	56.29

**** PLIST Processing complete ****

A3-39

Date 10/2/90

MAT 8230 C-GC-MS CONDITIONS

Column HP-5 50m x 0.2 mm 0.33 µm film

Injector 250°C Splitless 30 PSI He

GC Oven Program 160°C (2 min) 25°C/min 270°C (20 min)

Separator 280°C (755)

Line of Sight 290°C (770)

Ion Source EI / 200°C / 1mA / 70eV

Ua/Ub 815

Y1 466

Y2 603

X1 522

X2 497

L1 454

L2 418

S1 0.2

Z1 549

Z2 550

P 541

Filter 330 Hz

Multiplier 2.1 KV (500)

MSCHAR 200:10:40:25:6:131000

HR Slits S-586 C-582 Resolution 7000

LR Slits S-594 C-804 Resolution 1000

HR : Ion 331 Resp.(V) 1.5 V LR : Ion 331 Resp.(V) 15 V

LR/HR Resp. 10

A3-40

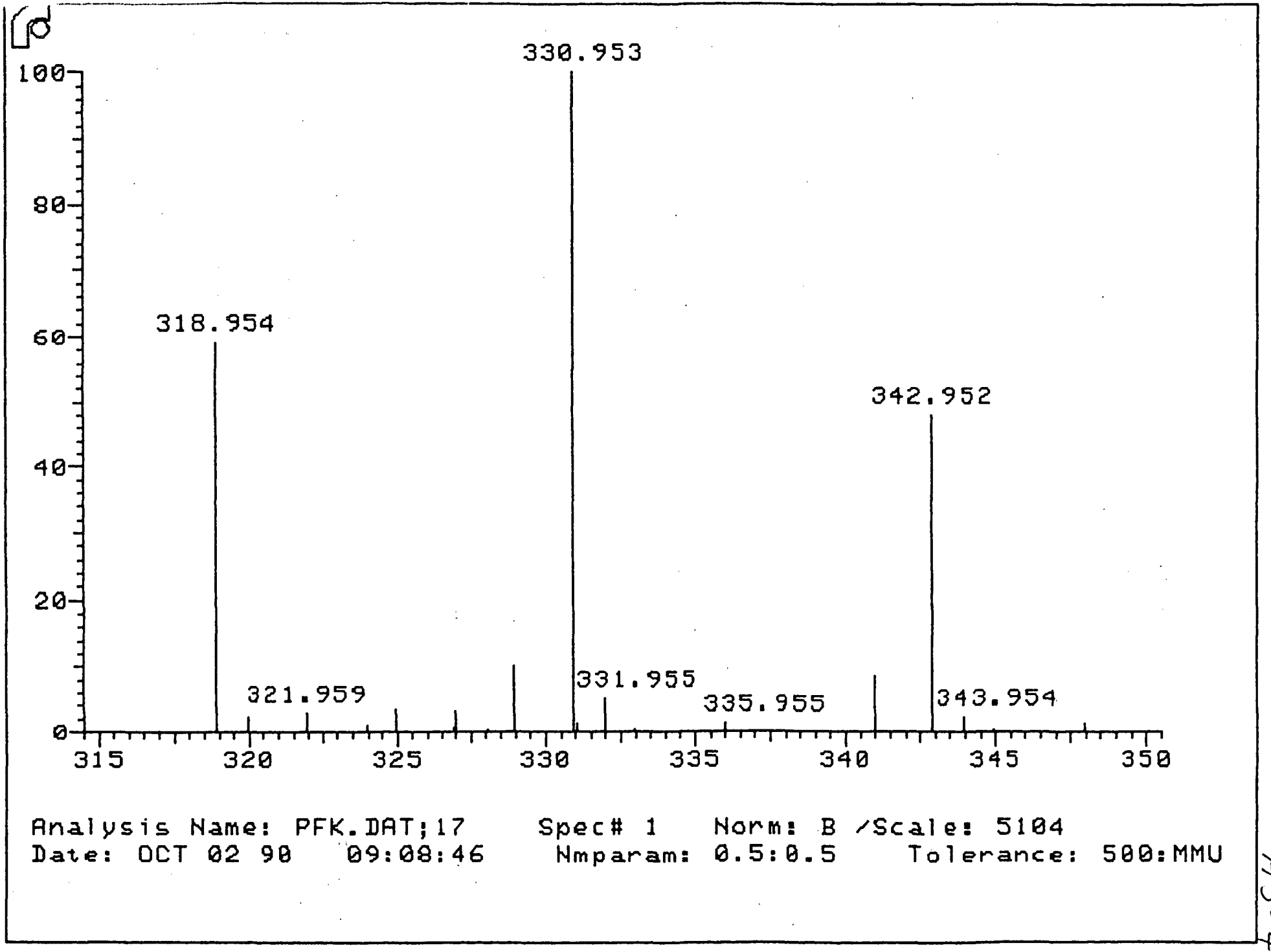
SSX: SLIST of DM00:[300,303]PFK.DAT;15
Finnigan MAT Oct 2 90 09:06:12 Page: 1

Spectrum Number: 2
Number of Peaks: 275

Norm. Factors: 1. 1703.20

PEAK#	MASS	A	B
41	65.1094	2304.	1.35
43	69.0312	78384.	46.02
47	71.1250	3296.	1.94
59	85.1094	1968.	1.16
62	91.0937	16928.	9.94
63	92.0938	11168.	6.56
71	100.0469	3584.	2.10
77	119.2188	21472.	12.61
81	131.0469	20768.	12.19
97	162.0469	2352.	1.38
99	169.0000	18496.	10.86
103	181.0000	17824.	10.47
108	193.0469	2992.	1.76
112	205.0312	1744.	1.02
114	207.0781	4624.	2.71
119	219.0156	10096.	5.93
123	231.0000	9344.	5.49
128	243.0469	4368.	2.56
134	255.0000	1952.	1.15
141	269.0313	4944.	2.90
146	281.0469	8016.	4.71
154	292.9688	2544.	1.49
167	319.0156	2416.	1.42
170	331.0469	4992.	2.93
175	342.9531	3808.	2.24
186	381.0000	3360.	1.97
200	430.9687	2784.	1.63
209	480.9844	1936.	1.14

***** SLIST processing complete. *****



Analysis Name: PFK.DAT;17 Spec# 1 Norm: B /Scale: 5104
Date: OCT 02 90 09:08:46 Nmparam: 0.5:0.5 Tolerance: 500:MMU

A3-42

SSX: MASSMENU TCDD7.MMN;2
Finnigan MAT Oct 2 90 09:09:16 Page: 4

Instrument: AP 0

Number of focussing steps was 0 jumping span was 100.0%

Menu is for a HIGH RESOLUTION ACQUISITION

Window number 1
from 19:00 to 25:00
Expected peak width is 0:12 cycle time is 1500.0 msec
Monitor 5 Channels

	Mass	Exp. Ints.	Samples	Group	
1	319.8965	1	16	1	
2	321.8937	1	16	1	
3	330.9793	16	1	1	L
4	331.9368	4	4	1	
5	333.9339	4	4	1	

(Window # 2 to 7 NOT ready for acquisition)

SSX: MASSMENU TCDD7.MMN;2
Finnigan MAT Oct 2 90 09:09:16 Page: 5

Beginning MASS MENU creation

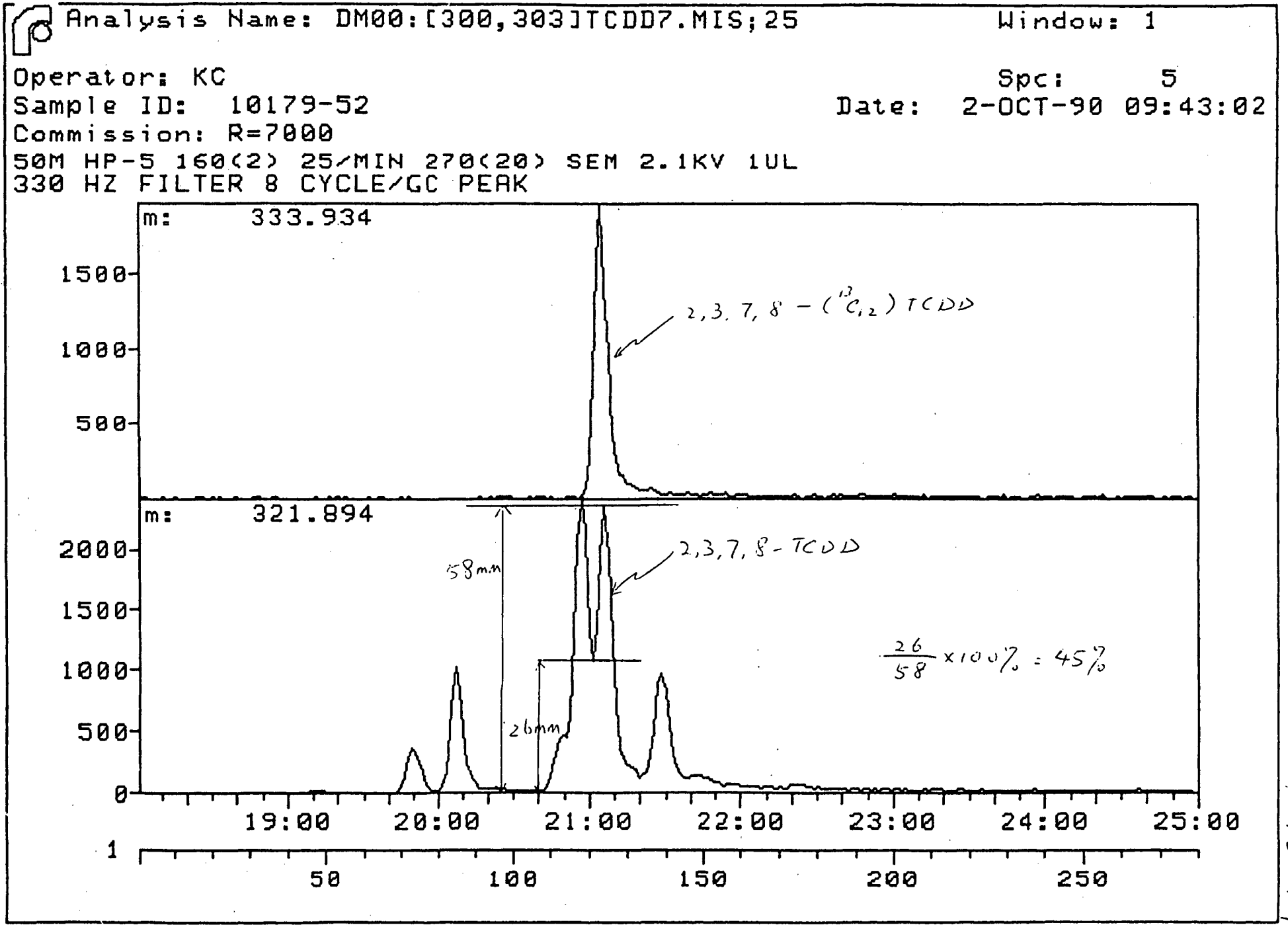
Magnet settle time 200 msec
Magnet jump time 1000 usec
Magnet focus time 40 msec
EDAC jump time 25 msec
EDAC focus time 6 msec
EDAC capabilities: rated = 131000, calibrated = 661619
used = 661619

Window number 1

from 2164 to 2734

MASS	MDAC	EDAC	DELDAC	NSTEP	NSUM	CYCTIME
47671	47671	120645	100012	24	0	2734
47771	0	173752	0	0	20	2734
50171	0	163756	0	0	20	2734
51277	0	120645	0	0	1	2734
51374	0	115166	0	0	4	2734
51574	0	105635	0	0	4	2734

***** MASS MENU Processing complete *****


Analysis Name: DM00:[300,303]TCDD7.MIS;25
Window: 1
Operator: KC
Spc: 5
Sample ID: 10179-52
Date: 2-OCT-90 09:43:02
Commission: R=7000
50M HP-5 160(2) 25/MIN 270(20) SEM 2.1KV 1UL
330 HZ FILTER 8 CYCLE/GC PEAK
m: 333.934
2,3,7,8 - ($^{13}C_{12}$) TCDD
m: 321.894
2,3,7,8-TCDD
58mm
26mm
$\frac{26}{58} \times 100\% = 45\%$
1500
1000
500
2000
1500
1000
500
0
19:00
20:00
21:00
22:00
23:00
24:00
25:00
1
50
100
150
200
250

A3-44